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Studies of Surface Films Formed by Adsorption of Polar Organic Molecules on Activated Metal Surfaces

Roy Leo Bennett
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To the Graduate Council:

I am submitting herewith a dissertation written by Roy Leo Bennett entitled "Studies of Surface Films Formed by Adsorption of Polar Organic Molecules on Activated Metal Surfaces." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Hilton Smith, Major Professor

We have read this dissertation and recommend its acceptance:

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

December 9, 1959

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Major Professor

We have read this dissertation
and recommend its acceptance:

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Accepted for the Council:

Dale Stanley
Dean of the Graduate School

33

STUDIES OF SURFACE FILMS FORMED BY ADSORPTION OF POLAR ORGANIC MOLECULES ON ACTIVATED METAL SURFACES

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

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by

Roy Leo Bennett

December 1959

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TABLE OF CONTENTS

CHAPTER PAGE

CHAPTER PAGE

CHAPTER PAGE

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

A. Background

The investigation of adsorption has been a valuable aid in understanding the properties of metal surfaces. The surface of a metal differs from the interior of the material due to unsatisfied valence forces which impart an affinity for adsorbed materials. This high surface energy is illustrated by the fact that when two clean metal surfaces are placed in contact, that is, when there is no intervening adsorbed film, cold welding results. The resulting bond is equivalent to the bonding in the rest of the metal. This has been demonstrated by Bowden and Young,[1] who showed that mere contact of iron, nickel, and platinum surfaces, which had been cleaned in vacuo, resulted in seizing and welding. Since adsorbed films destroy this property, adsorption is important in friction and lubrication phenomena.

Lubrication may be divided into two basic types. One, hydrodynamic lubrication, results when the fluid film exceeds the maximum height of the asperities of the surface. This is not a surface phenomenon. On the other hand, when the film of the lubricant is so thin that the surface roughness makes itself felt, the behavior of the lubricant is not determined by its viscosity but by the properties of the film on the surface. This is called boundary lubrication. The best known boundary lubricants are soaps. Often fatty acids are employed since they, under the proper conditions, will react with metallic

surfaces to form the soaps in situ. The action of boundary lubricant films has been shown by Rabinowicz and Tabor,[2] who used an autoradiographic technique, to be relatively simple. When the lubricant film is solid, the greater part of the load is borne by the film itself. However, there is some penetration of the film by surface asperities. Thus, there is a small amount of metallic interaction, but since most of the shearing is of the lubricant, the metal transfer is low. If the temperature is raised until the film melts, the film loses its rigidity and there is an increased metal interaction, hence metal transfer. Since fatty acids react to form high melting metallic soaps, they are superior to paraffins and alcohols.

In addition to lubrication, other surface effects dependent on adsorption are catalytic activity and corrosion resistance. An essential step in heterogeneous catalysis is the adsorption of one or more of the reactants. Many investigators of catalytic behavior believe that there is a non-uniformity of the catalyst surfaces, that is, there are active spots. These active spots, first proposed by H. S. Taylor,[3] might be such surface irregularities as phase boundaries, crystal corners or edges, or maybe some form of lattice imperfection. There is evidence that corrosion inhibitors are adsorbed on metal surfaces and appear to inhibit corrosion by the formation of a protective monolayer.

This study was undertaken with the objective of increasing the knowledge of the process which occurs when a metal is machined under an inert non-polar solvent containing a polar adsorbate. It is an extension of the work initiated by Smith and Allen[4] and advanced by McGill[5] and Fort.[6] The nature and extent of the adsorption, desorption, and

exchange of the adsorbate, as well as the condition of the metallic surface, should be of fundamental interest and, perhaps, suggest practical application.

B. Previous Work

1. Theoretical Aspects of Adsorption

a. Cross-sectional area and orientation of fatty acids. The idea has long existed that if a compound containing a long hydrocarbon chain attached to a polar group is placed on a water surface, a monomolecular film is formed. The polar group, having a high affinity for water, is absorbed in the liquid; the insoluble hydrocarbon portion is repelled. Langmuir,[7] using a film balance, found the cross-sectional area on water of palmitic acid to be 21 $Å^2$, while cerotic acid, which has 26 rather than 16 carbon atoms, was only slightly higher, 27 $Å^2$. Tristearin, with three hydrocarbon chains of 19 carbons each, was 66 $Å^2$, or about three times the value for a single chain. These measurements gave a definite indication that the molecules were oriented perpendicular to the water surface. The area of a long straight-chain carboxylic acid is virtually independent of the chain length. The measurements by Adam[8] show that the area of a number of long chain fatty acids above 12 carbons in length is about 21 $Å^2$.

These values were obtained on pure water; however, when slightly acid solution was the subphase, the compression of the film begins at a value of about 25 $Å^2$. The most plausible explanation is that in pure water the molecules penetrate the water to slightly varying depths;

consequently, the cross section of the hydrocarbon chain rather than the carboxyl group determines the area. With the acid subphase the carboxyl groups are forced out of the liquid to the same depth. Thus, the larger carboxyl group determines the area at which resistance to compression begins. The system in which a fatty acid reacts with a metal to form an oriented soap appears to be more analogous to the monolayer on the acidified water, since the carboxyl group probably determines the area in both instances.

b. Monolayer formation on metal surfaces. Bigelow, Pickett, and Zisman[9] and Bigelow, Glass, and Zisman[10] have studied the adsorption of monolayers on metal surfaces and have reached a number of conclusions regarding the mechanism of the film formation. There is a reversible diffusion of the molecules through the solution to the surface, where they are adsorbed in a close-packed, vertically oriented monolayer with polar ends attached to the metal. The film does not necessarily follow the contours of the metal surface, but may bridge over gaps which are of the order in size of the area of the molecule. For molecules which contain unsaturated bonds, adsorption takes place at the point of unsaturation as well as at the polar group. As a result, the molecule lies flat on the surface.

Carboxylic acids exist to a large extent as dimers in hydrocarbon solution. Dielectric constant measurements[11] indicate that at a molar concentration of 10^{-3}, about 50 per cent of the acid is in the dimeric form. Even at concentrations of 10^{-6} M., which is in the range used by Zisman and in this study, the dimer probably exists to the extent of a few per cent. Frewing[12] reached the conclusion that the fatty acid was

adsorbed as dimer. Zisman,[9] however, suggests that this is not the case, but that monomers are adsorbed and replaced in solution by an equilibrium between the two forms.

2. Adsorption on Metal Powder

Since finely divided metals provide large surface areas, they are employed extensively as catalysts. Consequently, a large portion of the studies on metal has been with powders. For example, Cook and Hackerman[13] have investigated the adsorption of stearic and capric acids on iron powders. They found that as the concentration of the acid in contact with powder increased, the amount adsorbed increased. After the powders had adsorbed the acid, they were washed with benzene. It was found that regardless of the amount adsorbed, essentially the same residual amount was left after rinsing. Smith and Fuzek[14] studied the adsorption of fatty acids on two widely used catalysts, Raney nickel and Adams' platinum. They concluded that the adsorption was irreversible. Using the cross-sectional area of the fatty acids, the specific areas of the powders were calculated.

The large area available on powders allows the use of macro or semi-micro analytical techniques. There are a number of disadvantages, however. Their production involves rather strong physical or chemical treatment, and as a result the surface is often contaminated. Films such as the oxides, hydroxides, or hydrides are apt to be present. In addition, it is sometimes difficult to reproduce the same surface characteristics from one batch to another.

3. Adsorption on Gross Metal Surfaces

When adsorption on gross metal surfaces is studied, the surfaces available are so small that extremely sensitive analytical techniques are required. Occasionally the adsorption process can be followed by some physical property which changes drastically as the surface is covered. Such an example is the contact potential. Indirect methods must be interpreted with caution, however.

a. Oleophobic films. In 1946 oleophobic layers were first reported by Bigelow, Pickett, and Zisman.[9] They found that metal samples could be dipped into solutions of eicosyl alcohol in hexadecane and removed unwetted. When they were dipped into pure hexadecane, they emerged with oily surfaces. Contact angle measurements were used to investigate the adsorption. A variety of these oleophobic films were found and the conditions required for their formation were established. The adsorbate must have a long chain with a polar group on one end and a methyl (or other non-polar group) on the other. Also, it must have a relatively low solubility in the solvent.

Electron diffraction studies[15] have shown that adsorbed stearic acid molecules are not oriented perfectly vertically, but are tilted 5° from perpendicular to the surface. Epstein[16] has interpreted electron micrographs to indicate that the monolayer is in clusters, with the central molecules oriented vertically and the surrounding ones leaning toward the center. This, he believes, is due to the greater size of the end carboxyl group relative to the long chain.

b. Mixed monolayers. The recent electron microscope investigation of oleophobic monolayers by Mathieson[17] is interesting. He retracted

a Langmuir-Blodgett monolayer on mica from a stearic acid solution in hexadecane. The electron micrograph indicated that the stearic acid was clustered in islands covering about one-third of the surface. The lack of complete coverage was apparently not due to evaporation, since a monolayer retracted from a stearic acid melt did not show the island structure. In order to explain the oleophobic property when only a portion of the surface was covered, Mathieson suggested that hexadecane, the solvent, is incorporated in the monolayer. Since the hexadecane has a much greater vapor pressure than the stearic acid, it is pumped off during the preparation of the sample for the micrograph. The remaining acid molecules then collapse into the island structure. The postulated mixed monolayer has a close-packed hexagonal structure, with each hexadecane molecule having three stearic acid molecules among its six nearest neighbors.

Also recently, Cook and Ries[18] have combined experimental evidence from three different experimental techniques which indicates that fairly stable mixed films are rapidly formed on metal, mica, or water surfaces, and that these films contain fewer stearic acid than hexadecane molecules. The mechanism suggested is that the stearic acid molecules are first adsorbed in a widely scattered fashion. Each either is accompanied by six molecules of hexadecane or is immediately surrounded by them. The rest of the surface is covered by weakly adsorbed hexadecane which is quickly replaced by stearic acid as the latter diffuses to the surface. The hexadecane in contact with stearic acid is replaced less readily. Some is in contact in three acid molecules and is displaced with difficulty at room temperature.

The existence of mixed films of solute and solvent was suggested by Levine and Zisman,[19] but only where there is insufficient time for equilibrium to be established; that is, they were expected only as a transient state. Levine and Zisman felt that the mixed film could exist only when both the solvent and solute are paraffinic. Cook and Ries agree.

c. Other studies on unactivated surfaces. Dobry[20] has determined the amount of stearic acid adsorbed from benzene on copper and copper oxide. Metal foil was used and the adsorption measured with a microbalance. By desorbing the films into benzene, Dobry concluded that 30 per cent of the layer reacted to form soap on the oxidized surface, but none on unoxidized copper. Bowden and Moore,[21] in conducting a similar set of experiments, used a radioactive tagged copper sample onto which a Langmuir-Blodgett monolayer of stearic acid was placed. The monolayer was desorbed, and by a counting technique the reaction of acid with metal was found to be 25 per cent. Beischer[22] has studied Langmuir-Blodgett films tagged with carbon-14. The surface was analyzed by radiography. Desorption of the acid into benzene led to low results due to the small solubility of the soap in benzene, but it was estimated that 30 per cent reaction occurred on a surface which was not protected from oxidation.

Shepard and Rice[23] have studied the adsorption of carbon-14 labeled perfluorooctanoic acid from benzene onto glass, aluminum, and platinum samples. They found that the adsorption was not reversible. Desorption rates were found to increase with the polarity of the solvent. Some conclusions regarding the use of adsorption techniques in determining

surface areas of planar surfaces were reached. For metals which form no oxide or thin oxide films, i.e., platinum or gold, and for metals whose oxides are tough, compact films, i.e., aluminum, chromium, or nickel, surface data can be obtained. However, for those metals which form thick permeable oxide layers, such as cadmium, copper, or zinc, the data must be interpreted with caution.

4. Adsorption on Freshly Machined Metals

Common methods used to produce relatively smooth surfaces, such as mechanical polishing or electropolishing, subject the metal to very harsh physical or chemical treatment. Polishing leaves minute fragments of the abrasive material imbedded in the metal; while electropolishing is carried out under a strong chemical atmosphere. Both are obviously incapable of giving a surface representative of the pure metal.

a. Work of Smith and Allen. Smith and Allen[4] prepared a series of freshly machined surfaces which were cleaner than most which had been previously investigated. Two techniques were used. In one set of experiments the samples were machined under a nonadecanoic acid solution in cyclohexane. Adsorption of the acid, labeled with carbon-14, was observed to reach a constant value at a rapid rate. On the other hand, similar samples, machined in air, then placed in solution, adsorbed the acid continuously, with the rate dependent on the metal substrate. The amounts exceeded the constant level value obtained with the solution-machined samples. These investigators concluded that air-machined samples underwent an oxidation, and the reaction was then between the porous oxide and the acid. Solution-machined metal samples were assumed to attain a monolayer rapidly by reaction of the clean metal with acid.

b. Work of Smith and McGill. In a continuation of Allen's work, McGill[5] found that solution-machined samples of magnesium, lead, copper, nickel, and aluminum reached the same saturation limit of 4.17 molecules per 100 $Å^2$. This is extremely close to the value which Langmuir[7] obtained from force-area measurements for compressed fatty acids monolayers on acidified water surface. It appeared, then, that the metal was covered to the extent of just one close-packed monolayer.

When samples were machined under pure solvent, then aged for varying times before transferring to nonadecanoic acid solution, the ability to adsorb decreased with aging time. The rate of this decrease was found by McGill to be in accord with the decay of the Kramer effect. In 1947 Kramer[24] discovered that freshly abraded metal surfaces emitted negatively charged particles which could be detected by a Geiger point counter tube. The phenomenon of low energy electron emission, which Kramer called exo-electrons, has become known as the Kramer effect. McGill measured the Kramer activity indirectly by the Russell effect, which is the ability of the activated surface to darken sensitive photographic plates.

McGill suggested that the Kramer effect activated the fresh surfaces and furnished enough energy for the reaction of the acid with the metal substrate. He demonstrated the presence of soap formation by desorbing the film and analyzing the amount of metal in the desorbing solution. The amount found agreed well with the theoretical amount except for gold and platinum where no metal was found. It was concluded that on these two metals, which do not attain a full monolayer, the films were physically adsorbed. The rate of removal of the adsorbed

film was found to be proportional to the solubilities of the respective soaps, not the fatty acid.

c. Work of Smith and Fort. Fort[6] extended the work on freshly machined metals by studying the adsorptive behavior of additional metals in hopes of elucidating the adsorption mechanism. Aluminum was particularly interesting because of the difficulty with which it formed a film despite its high activity. Cobalt and indium were found to attain monolayers but, for the latter metal, with some difficulty, so that only with the more concentrated solutions was a full monolayer equivalent reached. This was somewhat surprising, since free energy requirements were not as high as for copper or silver which do form monolayers more easily. The behavior of tin was also anomalous. Considerably less than a monolayer was adsorbed, and the isotherms were similar to gold and platinum, with the coverage reaching a maximum after ten minutes and becoming less after longer exposure times. It was hypothesized that the low adsorption on aluminum, indium, and tin might be due to high solubilities of their soaps with resulting fast desorption rates.

With the use of radioactive exchange measurements, Fort established that the monolayer was not a static film, but that it was continually being renewed. For this exchange to occur, there must be a gradual build-up of metal in the desorbing solution. This soap-desorbing rate was measured by analytical determinations of the metal in the solution. The order of the rate of the exchange was aluminum > copper > silver. The kinetic data from the radioactive exchange and the soap desorption were treated mathematically with the assumptions that the rate-determining step of the exchange was the

desorbing rate and the surface was uniformly active. With all three metals the resulting rate constants indicated that the soap desorption was far greater than would be expected. Smith and Fort[25] suggest that the treatment fails because the surface is not uniform, but there are active sites upon which adsorption and desorption occur more rapidly than others.

CHAPTER II

EXPERIMENTAL APPARATUS AND METHODS

A. Machining Equipment

1. Lathe

The softer metal samples were machined by the same techniques used by Allen,[4] McGill,[5] and Fort.[6] A South Bend 24-inch metal turning lathe was modified to serve as a manual planing instrument. The apparatus is shown in Figure 1. The compound rest top with tool holder was removed from its base and mounted vertically above the lathe bed on 4-inch channel steel. The sample holder, containing the metal sample with cup, was mounted on the lathe carriage so that a cut could be made by moving the carriage under the fixed tool. The position of the cut was adjusted by the cross feed micrometer on the carriage; the depth, by the vertical feed micrometer. Slices 100 mils wide were taken when a quarter-inch tool was used. After the tool was passed across the sample surface, it was transposed around the sample rather than back over the fresh cut. Movement of the carriage was manual, not motor driven, since Allen found this produced the most satisfactory surface. For 1.5-inch diameter samples, ten passes were required with the quarter-inch square tool. A standard cutting time of one hundred seconds was adopted in accord with previous work.

2. Milling Machine

Tough metals such as iron, cobalt, and nickel could not be machined satisfactorily on the lathe. For these metals, end-milling

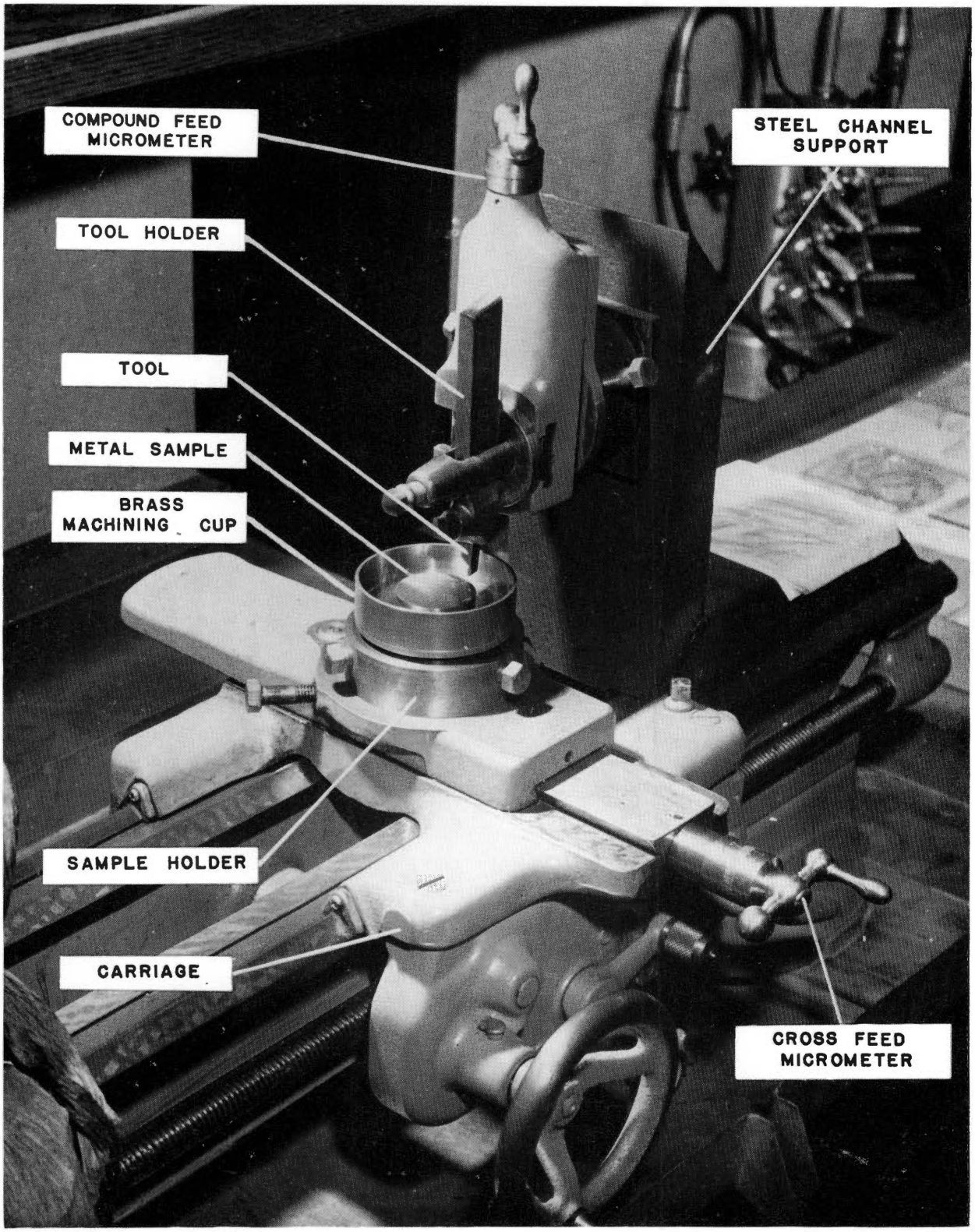


FIGURE I
MACHINING APPARATUS

appeared to be more effective. At an early stage in the work an attempt was made to convert an Atlas Clausing 18-inch heavy duty drill press with hand feed for milling purposes. An Atlas W68 universal compound vise was bolted to the drill press table. The vise had two cross feed screws that allowed the sample to be moved in both transverse and cross-wise directions. While this set-up gave excellent surfaces with the softer metals, there was too much "play" in the vise and, as a result, the end mill grabbed and chewed circular patterns in the tough metals.

A far superior milling apparatus was obtained later. A vertical milling attachment was ordered and installed on a Burke No. 4 milling machine. In order that the same metal sample might be used interchange-ably on the lathe or milling machine, a 4-inch diameter steel disc 1 inch thick was bolted to the table of the machine. The disc had a 1-3/8-inch hole in the center which served as a receptacle for the sample holder fitting. Table movement transverse to the operator was pneumatically operated with compressed air. This was adjusted so that the end mill made a complete pass across the metal and returned in ten seconds. A four-flute, quarter-inch end mill was used at a speed of 1100 r.p.m. During a return pass across the freshly cut surfaces, the sample was lowered with the vertical micrometer wheel so that the end mill did not contact the new surface. After the sample was cleared, it was returned to its original level. If this were not done, the surface would have been roughened considerably on the return pass. A new slice was made by turning the horizontal micrometer 200 mils forward before the next pass. Eight passes were required to machine the 1.5-inch-diameter samples.

3. Cutting Tools

For most work, the cutting tool was the same as used by Allen,[4] McGill,[5] and Fort.[6] A quarter-inch square Rex AAA cutter bit was ground and mounted in a straight tool holder. In preparing the tool, the top of the cutting edge was hollow-ground to a 3/16-inch radius. When the tool became dull, it was resharpened on the bottom with a fine oilstone and on the top with a 3/16-inch dowel wrapped with oil-soaked #400 carborundum paper. Care was taken in resharpening the tool in order to avoid changing the clearance angle. No one tool shape was found ideal for all metals machined, so the best conditions were established for each metal by trial and error. However, one of the principal nuisances, chatter, was prevented by obtaining a slicing rather than scraping action. The best surface was produced by a slicing tool, accompanied by long continuous curls of swarf. This was usually obtained by having the correct side rake and clearance angles, about 45° and 5°, respectively.

With some metals a cutting-off tool with a 3/32-inch cutting edge was used. This type tool sometimes gave better cuts, apparently due to its greater rigidity. Because of the smaller cutting edge, the number of passes was increased from 15 to 30. For the milling operation a variety of milling tools were tried at various speeds. A Morse high-speed, four-flute, quarter-inch end mill was found to be most suitable.

B. Metal Samples

1. Sample Mounting

A diagram of the sample holder is shown in Figure 2. All samples were mounted in steel holders which had beveled fittings that were

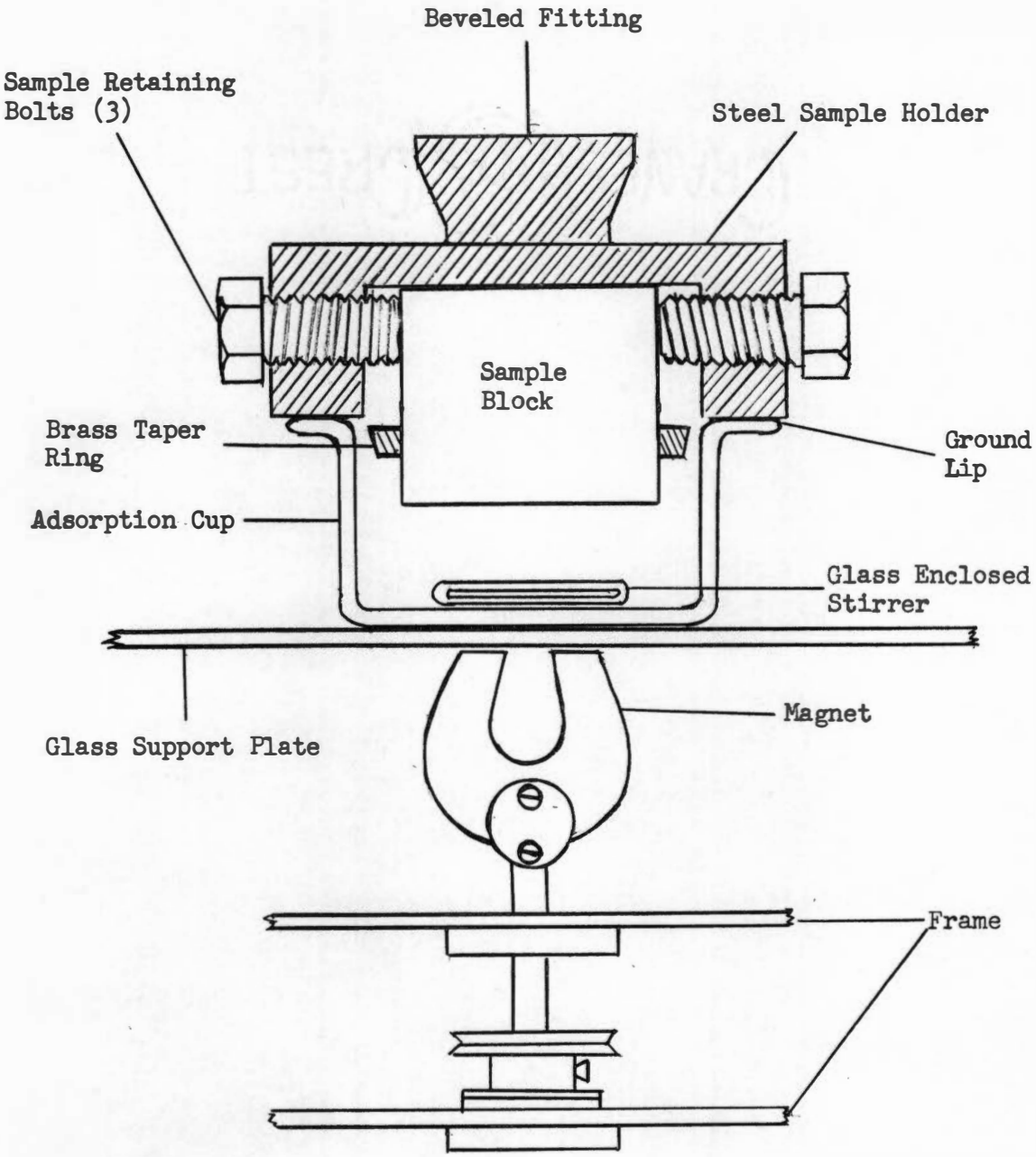


FIGURE 2

METAL SAMPLE HOLDER

AND ADSORPTION CUP

clamped into the receptacle of the lathe carriage or the milling machine table. The sample was held in place by three 3/8-inch machine bolts equally spaced around the sample block. If a large quantity of the material to be studied were available, the entire sample block was made of the metal. Metals which were available only in small quantities or in thin sheets were either soldered or cemented on the top of a sample block which was made of some cheaper material such as steel or brass. For low melting samples Eastman 910 adhesive was used to cement the working metal to the block.

The sample block had a brass 2° tapered ring soldered about 3/8-inch below the working surface of the sample. This received the brass machining cup which was used during the machining operation. The cup held the solvent or solution which covered the sample. At no time during this study was a lubricant such as Nonaq stopcock grease or glycerin necessary to prevent leakage between the cup and ring. The omission of these lubricants, which were used by Fort[5] and McGill,[6] eliminated the possibility of their contaminating the cyclohexane.

2. Sample Sources

During the course of this investigation ten metals were used in various studies: copper, magnesium, lead, tin, cadmium, bismuth, steel, titanium, vanadium, and zinc. The first four have also been used by either Allen,[4] McGill,[5] or Fort.[6] The purity of all ten has been determined by spectrographic analysis and the results are reported in Table I.

a. Copper. The entire sample block was made from a bar of commercial electrolytic copper. A very smooth surface was obtained from lathe-machining. Caution had to be taken in order to avoid spading and

TABLE I

SPECTROGRAPHIC METAL ANALYSES

	Metal Sample										
Impurity	Cu	Mg	Pb	Sn (old)	Sn (new)	Cd	Bi	1020 Steel	Ti	V	Zn
Ag	0.002	--	0.02	0.001	--	0.002	--	--	--	--	0.0005
Al	0.001	0.001	--	--	0.01	--	--	--	--	--	0.0005
Bi	--	--	--	0.01	--	--	strong	--	--	--	--
Ca	--	--	--	--	--	--	--	--	0.003	--	--
Cd	--	--	--	--	--	strong	--	--	--	--	0.03
Cr	--	--	--	--	--	--	--	0.1	0.003	--	--
Cu	strong	0.002	0.05	0.03	0.03	0.0005	--	0.03	0.03	0.001	0.0005
Fe	0.05	0.02	0.005	0.03	0.1	0.005	--	strong	0.1	0.001	0.05
Mg	0.005	strong	0.001	--	--	0.0005	--	--	--	--	0.002
Mn	--	0.002	--	--	--	--	--	0.2	0.02	--	--
Mo	--	--	--	--	--	--	--	0.05	--	--	--
Ni	0.003	--	0.003	0.002	0.05	0.005	--	0.05	0.05	--	0.03

TABLE I

SPECTROGRAPHIC METAL ANALYSES (continued)

	Metal Sample										
Impurity	Cu	Mg	Pb	Sn (old)	Sn (new)	Cd	Bi	1020 Steel	Ti	V	Zn
Pb	--	--	strong	2.5	0.05	0.01	--	--	--	--	0.01
Si	0.02	--	--	--	0.05	--	0.01	0.03	0.03	0.001	--
Sn	--	--	0.01	strong	strong	--	--	--	--	--	--
Ti	--	--	--	--	--	--	--	--	strong	--	--
V	--	--	--	--	--	--	--	--	--	strong	--
Zn	--	--	--	--	--	--	--	--	--	--	strong

Note: Amount reported is in per cent and may vary from one-third to three times the true value. All other metals were reported absent.

tearing. This occurs when too deep a cut is made. Once the surface is marred, considerable time is required to remove the damage.

b. Magnesium. The magnesium sample, obtained from the Dow Chemical Company, was machined into a 1.5-inch sample block and a brass taper ring was soldered to it. While the magnesium machined easily on the lathe, the sample contained large crystals, and the turnings tended to break into very small fragments.

c. Lead. This was ordinary chemical lead which gave extremely smooth surfaces. A 3/32-inch thick disc was soldered onto a brass sample block which held the tapered brass ring.

d. Tin. Two samples of tin were used. The first, used by Fort,[5] was obtained from the Division Lead Company. It was soldered to a sample block and, upon machining, yielded excellent surfaces. However, this sample contained a fairly high percentage of lead and exhibited some unexpected results. Consequently, a new, purer sample was obtained from the same source.

e. Cadmium. A 1/16-inch sheet of pure cadmium metal was purchased from Belmont Smelting and Refining Works of Brooklyn, New York. Discs 1.5 inches in diameter were cut and cemented with Eastman 910 adhesive to steel sample blocks. Cadmium machines easily and gives a very satisfactory surface.

f. Bismuth. A sample of bismuth was obtained from United States Smelting and Refining Company of New York, New York, and cemented on a steel sample block. Attempts to machine bismuth satisfactorily were unsuccessful, since the metal is very brittle and fractures into fine particles.

g. 1020 steel. The entire sample block was constructed from 1.5-inch steel rod. The material was very tough and difficult to machine on the lathe. Most of the work was done with the milling machine. Only a fair surface was produced.

h. Titanium. A sample of DuPont titanium was found to be easily machined by both the lathe and milling operations. The sample, a 1/8-inch thick disc, was cemented with Eastman 910 adhesive to an aluminum sample block.

i. Vanadium. Samples of pure vanadium buttons were obtained from Electro Metallurgical Company of Niagara Falls, New York. The buttons were machined down to discs 32 mm. in diameter. These were cemented to a nickel base. The vanadium tore very easily, so it could not be machined on the lathe. With the end mill, the metal turnings tended to adhere to the surface, but the cutting appeared satisfactory otherwise.

j. Zinc. A 1.5-inch zinc rod from the Belmont Smelting and Refining Works of Brooklyn, New York, was used to make the sample block. Machining the sample on the milling machine produced fine powder which led to complications. A series of narrow cracks was observed radiating from the center of the sample. When the quarter-inch square tool was used on the lathe, the metal cut easily enough but the cracks became enlarged. This disturbance was reduced when the cutting-off tool was employed.

C. Solution Preparation

1. Solvent Purification

Cyclohexane was the only solvent used in this study. Although most investigators have used other solvents, cyclohexane was chosen because of the following considerations: Allen,[4] McGill,[5] and Fort[6] used this solvent, and it was desired to compare this study with their results. Allen originally selected cyclohexane over benzene because of several advantages. Because cyclohexane contains no double bonds, there is a smaller probability of bond rupture in the neighborhood of the cutting tool where high temperatures are produced. Cyclohexane should not be as strongly adsorbed on the metal. It is also true that oxygen is less soluble in saturated hydrocarbons than in the corresponding aromatics.

Other properties of cyclohexane which favored its selection are its volatility, low cost, and inertness toward the solute and metals. The low cost plus the fact that it is easily purified are important, since large quantities were used. Another consideration in solvent selection is that cyclohexane would not be expected to form mixed monolayers which have been observed with long chain paraffinic solvents.[17,18]

Since cyclohexane is prepared commercially by the catalytic hydrogenation of benzene, this is the principal contaminant. Because the boiling points of benzene and cyclohexane are separated by only 0.6°, purification by distillation is not possible. McGill[5] has reviewed the methods which have been used to purify cyclohexane. He selected a nitration procedure as the most applicable to the quantities required.

Practical grade cyclohexane was first treated with nitric acid. This was followed by extraction with sodium hydroxide. The solvent was then dried over sodium amalgam and passed through an alumina column to remove polar impurities. The material passed the test of Zisman,[26] who found that when a drop of nonpolar solvent is placed on a water surface below pH 3.0, spreading will occur if traces of polar compounds are present.

Fort[5] found that the nitration treatment could be replaced by a simpler procedure. Practical grade cyclohexane was fractionally distilled to remove water and other impurities whose boiling points are not near that of the solvent. The distilled material was passed through a four-foot column, the upper half of which was packed with Alcoa F-20 alumina and the lower with 100-200 mesh Davidson silica gel. The alumina is effective in removing polar material, while the silica gel takes up unsaturated impurities such as benzene. Fort collected the cyclohexane at the rate of one drop every six seconds. He checked the capacity of the column by periodically examining the product at the maximum ultraviolet wavelength absorbed by benzene. One packed column was found to be sufficient for several liters of cyclohexane. The method of purification used by Fort was employed throughout this work.

All purified solvent was redistilled over sodium amalgam immediately before use. The distilling apparatus is shown in Figure 3. The sodium amalgam (80 weight per cent sodium) was liquid at the boiling point of cyclohexane and provided a fresh active surface as it was constantly swept clean by the boiling cyclohexane. The distilled cyclohexane was passed through a 6-inch alumina column before it was collected.

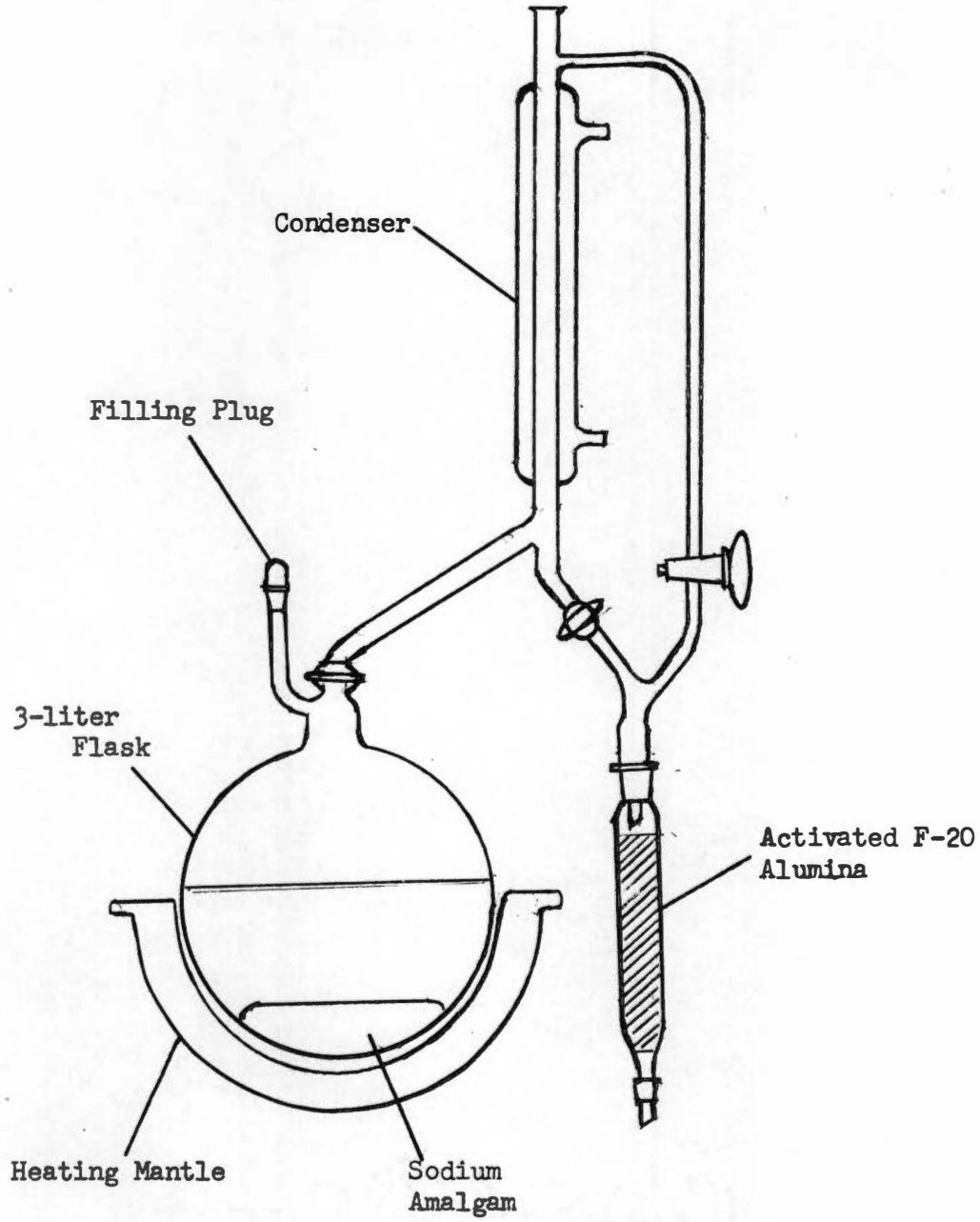


FIGURE 3

CYCLOHEXANE DRYING STILL

2. n-Nonadecanoic Acid

This long chain fatty acid was prepared by a Grignard reaction starting with octadecyl bromide and carbon-14 labeled barium carbonate. The apparatus and method are described in detail in Appendix I. Allen selected this acid, and it has been used by subsequent workers. The acid was labeled to the extent of 1.44 per cent. This gave convenient counts on the counting apparatus which was used to detect the soft beta radiation. Due to the long half-life of the isotope, 5568 years,[27] it is not necessary to make corrections for loss by decay. However, it has been shown by Lemmon[28] that electrons ejected during the decay may cause auto-decomposition. Since the beta radiation is weak, it is short-ranged, and therefore localized. Lemmon found that decomposition was greater than would be effected from radioactive decay alone; this was apparently due to chain decomposition. It was recommended that labeled compounds be stored in a diluted condition. For this reason stock solutions were prepared, rather than the pure acid stored.

3. Nonadecanoic Acid Solutions

A stock solution was prepared from purified cyclohexane and labeled n-nonadecanoic acid. This solution was designated "S" in agreement with Allen's nomenclature. From this solution, more dilute solutions were prepared as needed for adsorption, desorption, and exchange experiments. Losses due to adsorption on the walls of the glassware could have been serious if precautions were not taken. Accordingly, all flasks and pipettes used in preparing the dilute solutions were equilibrated. First, they were cleaned with hot chromic acid, rinsed several times with distilled, deionized water, and dried. Then they were rinsed,

while warm, with purified cyclohexane. They were allowed to stand for a week in contact with solution of the concentration to be used in them. Concentrations of the stock solution as well as the working solutions are presented in Table II.

For exchange measurements, solutions containing unlabeled n-nonadecanoic acid were prepared. A stock solution corresponding in concentration to the labeled "S" was designated "50 U."

4. Hexanoic Acid Solutions

A sample of 0.1 mc. of the sodium salt of hexanoic acid, labeled on the carboxyl carbon, was obtained from the Volk Radiochemical Company of Chicago. The salt was suspended in cyclohexane. Anhydrous hydrogen chloride was bubbled through the cyclohexane, but the salt would not dissolve until two drops of water was added. The mixture was evaporated to dryness over a steam bath. A stock solution was prepared by the addition of 500 ml. of cyclohexane. Radiochemical standardization indicated that some of the acid was lost, probably through co-distillation with cyclohexane. A solution approximating in concentration n-nonadecanoic acid "A" solution was prepared by dilution. This was designated solution "H."

D. Adsorption and Counting Equipment

1. Adsorption Cups

These cups were used as containers for the cyclohexane solution. They were made from the bottom inch of 150-ml. beakers. The edges were flanged and ground so that a tight seal was made between the inverted

TABLE II

CONCENTRATIONS OF WORKING SOLUTIONS

Designation		Concentration	
Labeled	Unlabeled	µg/ml.	M.
n-Nonadecanoic Acid:			
S	50 U	131.5	4.41×10^{-4}
2A	2 U	5.26	17.7×10^{-6}
A	U	2.63	8.83×10^{-6}
A/2	U/2	1.31	1.31×10^{-6}
n-Hexanoic Acid:			
HS		2.5	2.3×10^{-6}
H		1.0	9×10^{-6}

sample and the cup lip (see Figure 2). A seal was also made when a glass plate was placed over the cup. About 30 ml. of solution was required to contact the face of the inverted sample.

2. Stirring Board

An assembly of eight small magnets mounted on a frame and all driven at the same speed was used. The standard stirring rate was 140 r.p.m. Small magnetic stirrers, made by sealing short lengths of steel wire in glass tubing, were placed in the adsorption cups.

3. Counting Equipment

A Nuclear Instrument Company of Chicago model 165 scaling unit was used for all radioactive counting. The Geiger tube was a Tracerlab TGC-2 which was filled with helium and a quench gas at slightly reduced pressure. These tubes have thin mica windows of 1.6-1.8 mg./cm.^{2}, because the carbon-14 beta radiation is very weak. Operating voltages for the two tubes used were about 1350 volts. The tube was shielded with a 1/8-inch lead cylinder to cut down background radiation. The end of the tube was covered with an aluminum mask from which a 1-inch diameter circle was cut. The sample was placed on foam rubber cushion which provided a gentle pressure against the aluminum mask.

E. Experimental Techniques

1. Machining

Samples were machined by three methods, each of which allowed exposure of the freshly cut metal surface to a different environment. For air machining, the sample was cut in the presence of the room

atmosphere. In some cases it was desired to machine the sample under cover of the pure cyclohexane only. In such cases of solvent machining, the brass cup was attached and the solvent admitted until the sample surface was about a quarter-inch below the cyclohexane surface. When solution machining was done, the sample was covered to the same depth with cyclohexane - n-nonadecanoic acid solution. After the machining process was completed, the sample was quickly removed from the cutting machine and inverted over a waste beaker. The brass cup was removed and the sample with holder placed immediately on the stirred adsorption cup (Figure 2). This entire transfer operation was performed in only a few seconds, and the sample surface remained wet with adhering liquid during the transfer.

2. Adsorption and Counting

Just enough solution was poured into the adsorption cups to make good contact with the metal sample. Samples were exposed for varying times, with the recorded exposure time beginning as soon as the machining was started. When a sample was removed from the cup, a small amount of liquid adhered to the wetted surface. Evaporation of this would result in a count higher than that representing adsorbed molecules. Allen made a "drainage count" to correct for this. A clean air-machined sample was immersed in the acid solution and quickly removed before significant adsorption could occur. After draining the sample, he counted the sample and added the resulting figure to the background count. The count was somewhat erratic, probably due to variation in room temperature, air currents, and slight adsorption. Nevertheless, the correction agreed with the calculated amount from the estimated

volume of liquid adhering to the sample. At any rate, the correction was not large, about 60 counts per minute.

The problem was simplified by McGill, who blotted the sample surface with a photo blotter as soon as it was taken from the solution. The solution did not have time to evaporate, and the adsorbed acid was not removed by the blotting. Fort used fresh soft tissue for blotting and also obtained very reproducible measurements. This was the procedure used in this work.

As soon as the sample was blotted, it was placed on the rubber foam pad. The counting tube was lowered until the mask was held firmly against the metal face. Fifteen minutes counting time was usually used.

CHAPTER III

EXPERIMENTS ON MACHINED METAL SURFACES

A. Introduction

The investigations reported here are extensions of the work of Allen,[4] McGill,[5] and Fort.[6] In analogous experiments with new materials, the experimental techniques of these previous workers have been followed in exact detail. Although the behavior of a variety of metals had already been studied, the anomalous adsorption characteristics reported by Fort on tin suggested that further work on different metals was desirable.

McGill found that the metals with which he worked fell into a fairly well-defined pattern. The most active metals, i.e., aluminum, magnesium, lead, and nickel, formed soap monolayers by reaction with the adsorbed n-nonadecanoic acid. Some less active metals also reacted, although the free energy requirements for the ordinary reaction,

Nonadecanoic Acid + Metal → Soap + Hydrogen ,

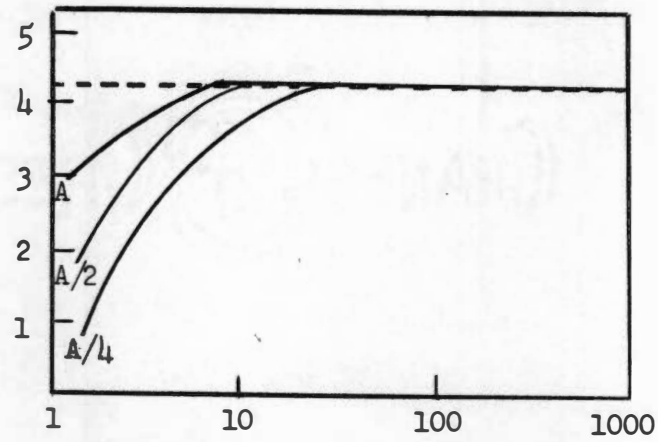
were not satisfied. Copper formed a full soap monolayer, and silver formed more than 90 per cent of a monolayer. The activation of the surface by machining, as shown by its Kramer activity, apparently supplied the required energy. For the inert metals, gold and platinum, McGill found that monolayers were not attained, but the adsorption isotherm showed a maximum, with the amount of adsorbed material becoming less for exposure times greater than ten minutes. Free energy calculations indicated that the required energy was above that available from

the Kramer effect. Analyses of desorbing solutions failed to show the presence of metal; therefore, it was concluded that acid was physically adsorbed on these inert metals.

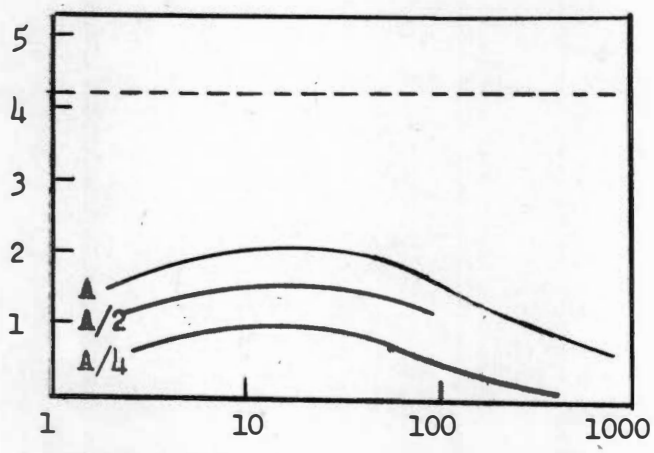
The only unusual trend that was revealed in McGill's adsorption isotherms was with aluminum (see Figure 4C). Although aluminum is a very active metal, only with the most concentrated solution, "A," was a full monolayer formed. This is in contrast to the other active metals and even some of the less active ones. McGill believed this to be due to steric resistance to the formation of the aluminum (III) soap. However, Fort found that indium, which should be less sterically hindered than aluminum, gave complete surface coverage with more difficulty. Tin attained only about 40 per cent of a monolayer equivalent and displayed an isotherm closely resembling those of gold and platinum (Figure 4B). Cobalt, as might be expected, adsorbed a monolayer.

The anomalous behavior of tin made further investigation worthwhile for two reasons. First, the tin sample used by Fort had a high lead content, 1.17 per cent; therefore, a new, purer sample was obtained. Second, the nature of the adsorbed film on tin had not been established. Being very active, tin should react to form a metallic soap film, but the nature of the adsorption isotherm indicated that this had to be proved.

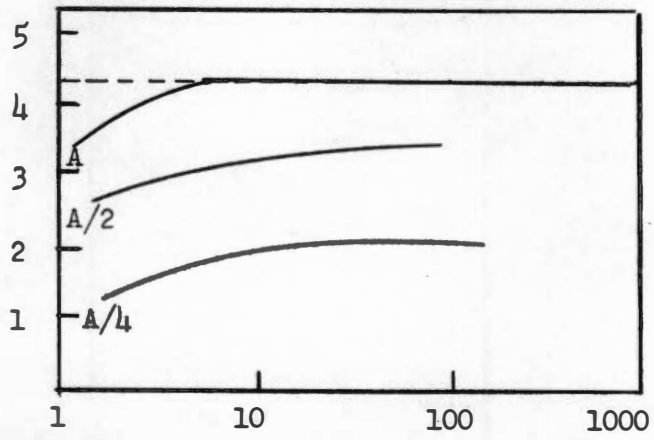
Previous machining techniques have not produced satisfactory surfaces on the harder metals. New cutting methods were sought, since many of the tougher metals are commercially important. Adsorption on these metals, as well as their behavior under conditions of exchange and desorption, would be valuable in expanding the data and conclusions reached by Fort regarding the non-uniformity of the metal surfaces.



A. Typical Isotherms on Active Metals



B. Typical Isotherms on Inert Metals



C. Adsorption Isotherms on Aluminum

FIGURE 4. McGILL'S ADSORPTION ISOTHERMS
Ordinate: Molecules per 100 Å^2
Abscissa: Exposure time in minutes
— — — represents monolayer

Another basic problem which has not been unequivocally answered is whether the monolayer films follow the contours of the metal surfaces, or bridge over the gaps, in order to form a smooth film. If the former is true, the metal must have a unit roughness factor. While this might be difficult to believe, it is consistent with the fact that a monolayer equivalent of metal is desorbed with the film. If, on the other hand, the film is bridging the irregularities, it is probably supported by the cohesive van der Waals' forces between the vertically oriented long hydrocarbon chains of the soaps formed at the surfaces. The adsorption of a short-chain carboxylic acid would probably tend to fit the surface contours more closely if this were the case.

B. Radiochemical Measurements and Standardization

Radioactive isotopes offer one of the most sensitive analytical methods available. Once a radioactively labeled film is deposited on a surface, it is then possible to determine the population density from the number of disintegrating carbon-14 atoms per minute. However, while the counts per minute observed with a Geiger-Muller tube are proportional to the number of disintegrations, several factors must be considered before a standardization can be made. Effects such as geometry and sidescattering have been made constant by having a fixed sample position against an aluminum mask. The tube counting efficiency and absorption by the tube window must be regarded attentively when the tube is changed. Standardization was always checked when a new tube was installed. Self-absorption of the radiation was observed to be unimportant in these experiments, since there was a monolayer or less present.

The largest factor affecting the observed counting rate was the backscattering by the various metal substrates.

When a carbon-14 atom on the surface of the metal disintegrates, the radiation is isotropically distributed. The portion of the radiation going upward strikes the counting tube window directly above it. A fraction of the radiation directed downward is reflected back up into the tube. This backscattering is much more pronounced with electrons than with heavier particles. The reflected intensity increases with metal thickness until the thickness becomes about one-third of the range of the electron saturation. In these experiments, the energy of the carbon-14 beta emission is so small (0.15 mev.) that the thickness of the metal sample is of no consequence. The backscattering factor has been shown to increase with atomic number[29] and surface roughness.[30,31] In general, a rough surface gives a higher reflection than a smooth one. Another consideration of weaker radiation, such as carbon-14 beta emission, is that the reflected particles which are scattered back to the counter are of lower energy than the directly emitted ones. Many cannot penetrate the mica window, so the observed effect is less pronounced than would be found with a windowless counter.

1. Experimental Procedure

Because of the difference in the backscattering factor of different metals, it was necessary to standardize each metal. The surfaces used in calibration were made as identical as possible to the experimental conditions. The following procedure was employed.

The metal was machined in the same fashion to be used in experiments under a pure cyclohexane cover. After the sample was blotted dry,

0.50 ml. of solution "A" was pipetted onto the surface. An inverted glass cup was placed over the sample for one hour, then removed. After the cyclohexane had evaporated, the sample was placed under the counter tube and the count observed. When the standard solution was pipetted onto the surface, the sharp edges around the periphery produced by the machining usually retained the solution on the surface. Occasionally the solution leaked over and the run was spoiled. The 0.50 ml. of "A" was satisfactory for most metals which were 1.5 inches in diameter. Some samples were smaller, so smaller volumes had to be used. For example, only 0.30 ml. could be pipetted onto a 3-cm. diameter tin sample without leakage.

This calibration procedure assumes that the radioactive acid is uniformly distributed over the face of the metal. This may not be entirely true. To correct for this possible error, several samples were run for each metal, and the counting tube mask was moved over different areas of the sample.

2. Results

The counts obtained with the metals used in this research are given in Table III. These were used to calculate the standardization factors which are tabulated in Table IV. The 1.5-inch diameter samples have a geometrical area of 11.4 cm^2. With this size sample, 0.50 ml. of "A" solution (8.83×10^{-6} M.) was pipetted onto the surface. The number of molecules per 100 $Å^2$ of apparent area would then be,

$$0.50 \times 10^{-3} \times 8.83 \times 10^{-6} \times 6.02 \times 10^{23} \times \frac{100}{11.4 \times 10^{16}} = 2.33 \quad .$$

TABLE III

ACID STANDARDIZATION COUNTS

	Tin	Copper	Titanium	Vanadium	Zinc	1020 Steel	Cadmium
Counts per minute:	518	702	758	535	848	741	938
	542	807	811	540	878	673	894
	523	779	816	579	806	701	933
	527	749	818	485	807	658	883
	580	770		611	882		
	536			531			
	508			535			
	514						
	511						
Average	529	761	801	861	844	693	913
Area, $cm.^2$	7.07	11.4	11.4	8.04	11.4	11.4	11.4
Solution volume, ml.	0.30	0.50	0.50	0.40	0.50	0.50	0.50
Machining technique	lathe	lathe	lathe	end mill	lathe	lathe	lathe

TABLE IV

STANDARDIZATION FACTORS

Metal	Population Density per 1000 counts/min., molecules per 100 $Å^2$	Monolayer Equivalent, counts/min.
Tin	4.27	976
Copper	3.06	1362
Titanium	2.91	1433
Vanadium	4.84	861
Zinc	2.76	1511
1020 Steel	3.36	1241
Cadmium	2.55	1634

If, as in the case of copper, 761 counts/min. were observed, the number of molecules per 100 $Å^2$ corresponding to 1000 counts/min. would be,

$$2.33 \times \frac{1000}{761} = 3.06 \quad .$$

From the cross-sectional area of a fatty acid molecule, it is known that a monolayer has 4.17 molecules per 100 $Å^2$, so the counts equivalent to a monolayer would be,

$$\frac{4.17}{2.33} \times 761 = 1362 \text{ counts/min.}$$

By way of comparison, it might be noted that McGill obtained 1357 counts/min. for a monolayer equivalent on copper. Values obtained with titanium, vanadium, cadmium, and zinc should not be compared with the other metals, since these were found after a new tube was installed. The new tube counted 25 per cent higher than the previous one. Since the geometry was fixed and tube efficiencies do not usually vary significantly, the difference is presumed to be due to different window thicknesses. At any rate, no error was introduced, since standardization and experimentation on a given metal were done with the same tube.

C. Adsorption Isotherms

One of the first steps in the investigation of a metal was the determination of its adsorption isotherms. As soon as a machining technique was developed which produced a satisfactorily smooth surface and the metal was standardized for backscattering, its adsorptive behavior was observed. The general procedure was to machine the metal under n-nonadecanoic acid solution and transfer it to a stirred cup of acid solution, where it was left for varying exposure times. The sample was

removed and blotted dry with soft tissue before counting. A new surface was used for each point on the isotherm. The adsorption cups were not precisely thermostatted, but all runs were carried out at 25° ± 2°.

1. Adsorption on Tin

Fort has reported the adsorption isotherm on a tin sample which had a high lead content. The tin did not reach a full monolayer, and its isotherm exhibited a maximum, after about ten minutes exposure time, at approximately 40 per cent coverage. Because of this anomalous behavior and the lack of purity of Fort's sample, the isotherms were redetermined on a new, purer specimen. The results, shown in Figure 5, were an almost exact duplication of Fort's findings.

2. Adsorption on Titanium

The isotherms for adsorption of n-nonadecanoic acid on titanium were determined and are shown in Figure 6. From an "A" solution, about 35 per cent of a monolayer is the maximum adsorbed, if unit roughness is assumed. The amount of nonadecanoic acid coverage decreases with time. From a solution twice as concentrated, "2A," a full monolayer is still not obtained. Here only about 50 per cent of a monolayer is present after a three-minute exposure time, with the amount decreasing to 40 per cent in a six-hour period.

3. Adsorption on 1020 Steel

The adsorption isotherms have been determined for adsorption on 1020 steel. This material was used rather than pure iron because the highly purified metal was so tough that the available machining methods were not satisfactory. The surfaces on which the isotherms shown in

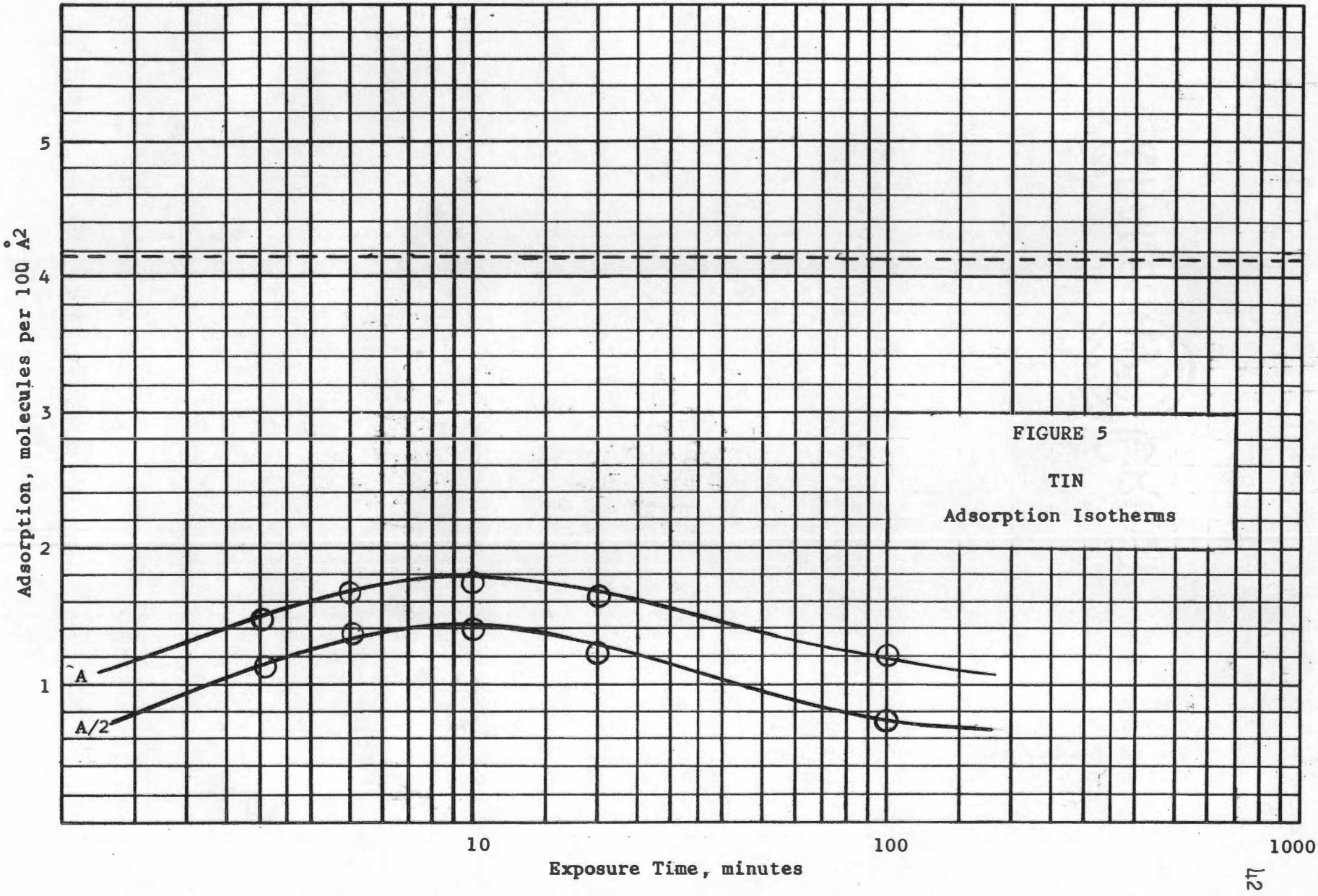


FIGURE 5

TIN

Adsorption Isotherms

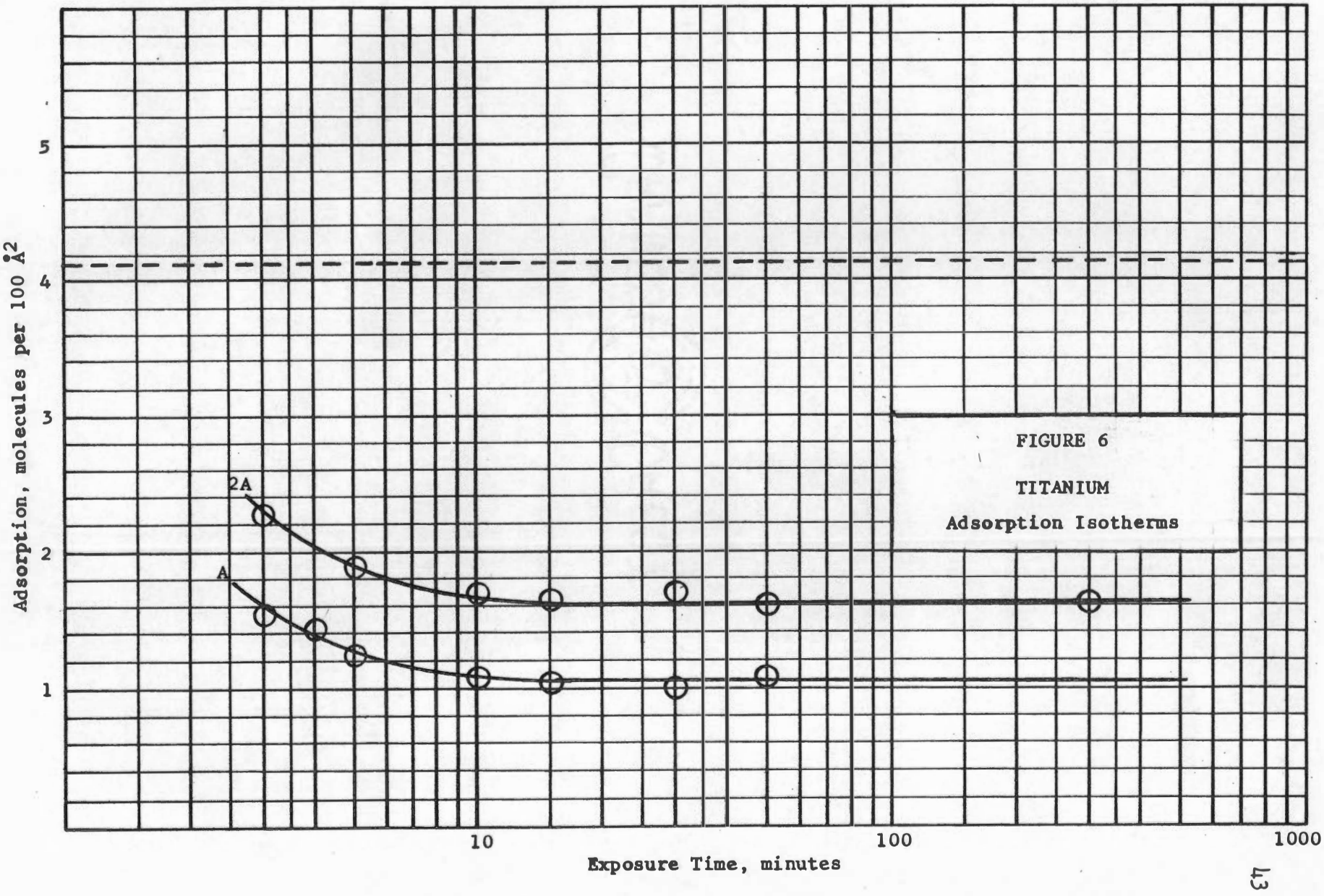


FIGURE 6

TITANIUM

Adsorption Isotherms

Figure 7 were obtained resulted from lathe machining, with the exception of one point. The adsorption from an "A" solution, after fifteen minutes exposure, onto an end-milled surface is shown to be consistent with the other data.

4. Adsorption on Cadmium

Cadmium was machined easily on the lathe, and adsorption of nonadecanoic acid on its surface was found by the standard procedure. On the basis of its high activity, cadmium would be expected to react to form soaps. The formation of a monolayer is confirmed by the adsorption isotherms (Figure 8).

5. Adsorption on Zinc

When the zinc sample was machined on the lathe, a pattern of deep fractures radiating from the center of the sample was observed. Machining on the milling machine gave a smooth, continuous surface which was thought at first to be more suitable. When adsorption measurements were made on the surface, high, erratic values were produced. After two hours exposure time, as much as 148 per cent of a monolayer was apparently on the surface. This was puzzling, since no more than a monolayer equivalent has yet been observed on "solution-machined" metals. It had been noticed that with end-milled samples an appreciable amount of metal powder was formed during the milling process. Some of this powder was unavoidably transferred with the sample to the adsorption cup. It is believed that the fine powder deposits on the surface, especially after long exposure times. Since the powder adsorbs a considerable amount of acid, the radioactive count of the sample would be raised.

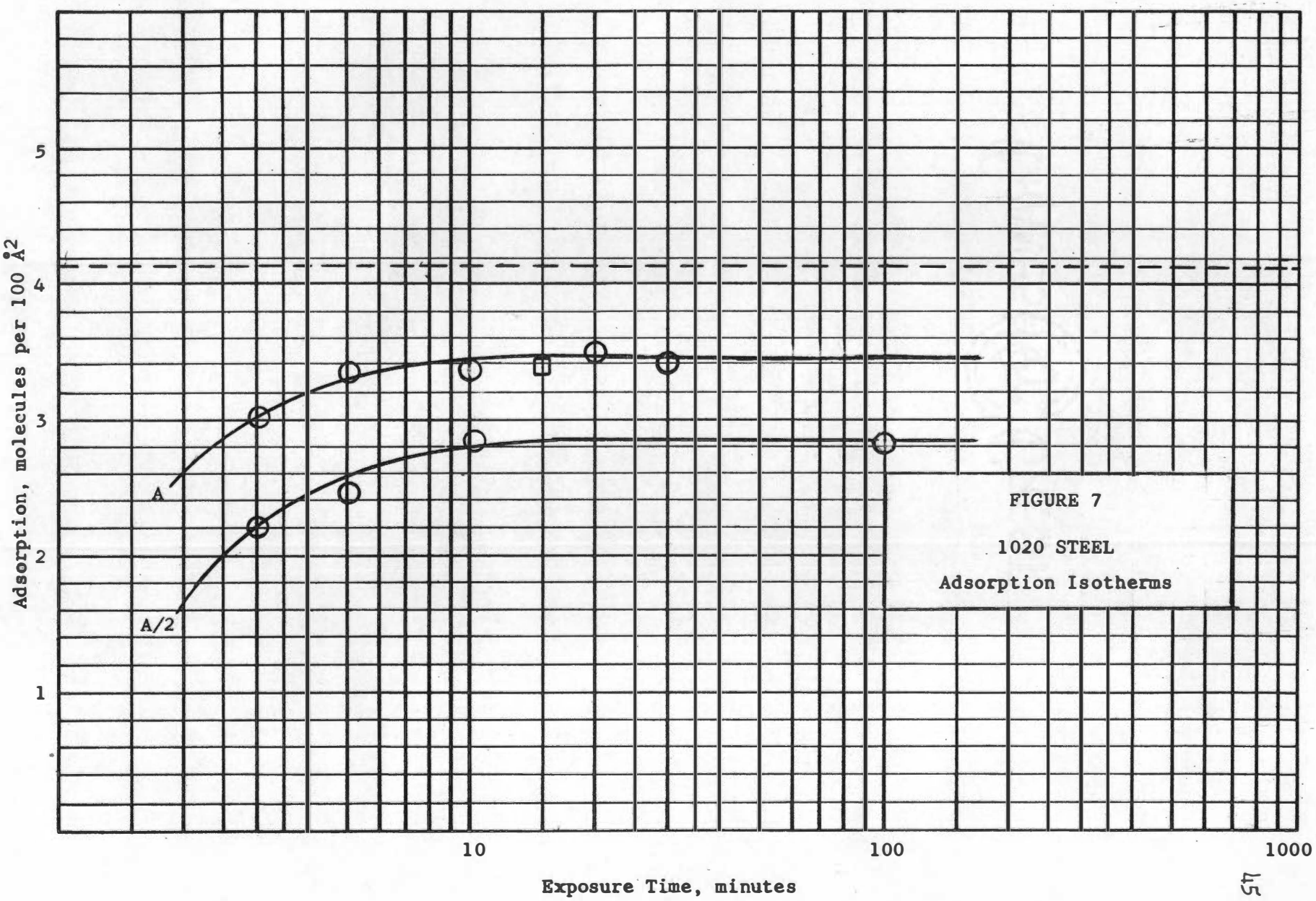


FIGURE 7

1020 STEEL

Adsorption Isotherms

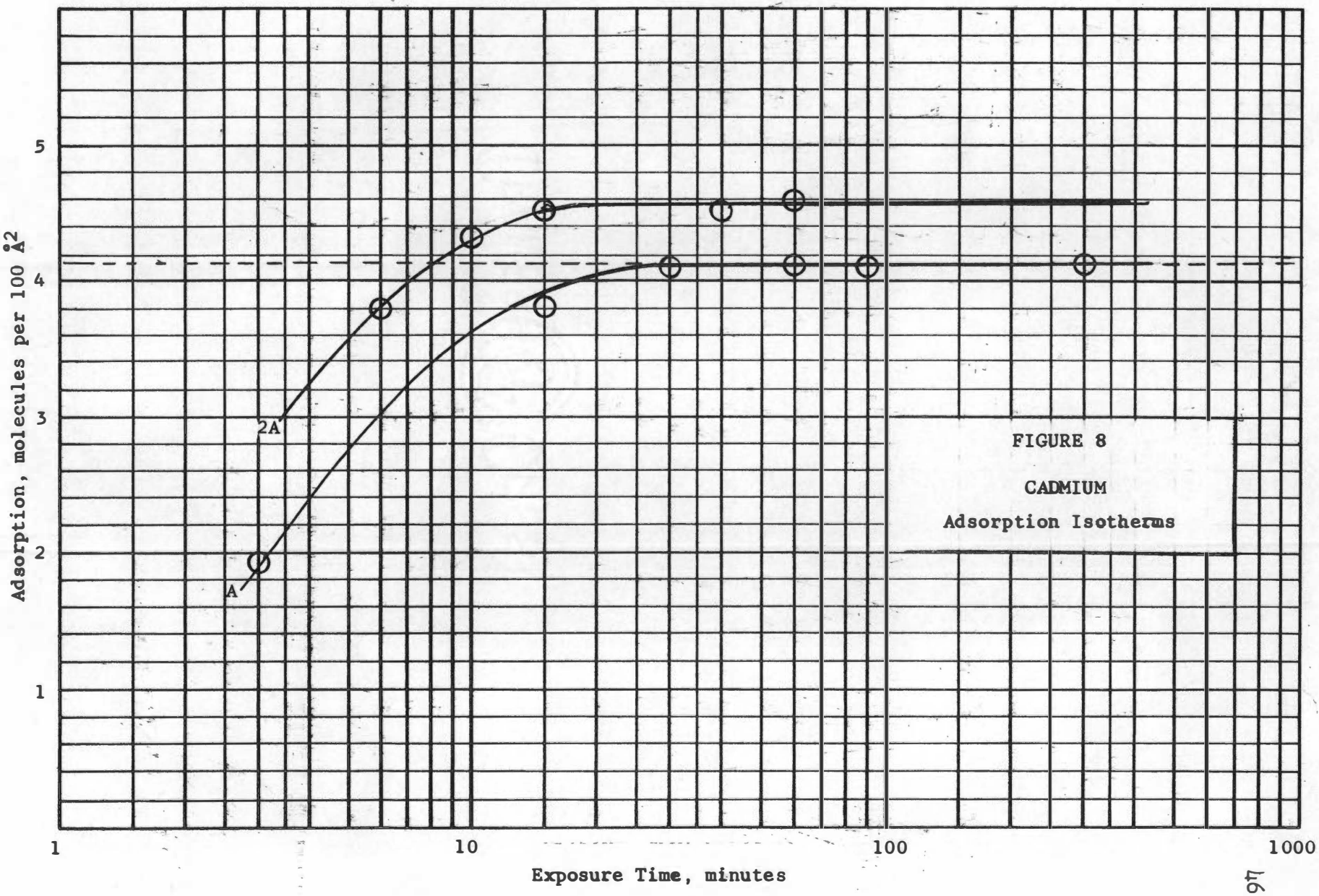


FIGURE 8

CADMIUM

Adsorption Isotherms

Evidence that the large count was due to adhering powder was obtained by rinsing the surface. The surface was covered with about 1 ml. of pure cyclohexane, then it was immediately blotted dry. This was done five or six times, with the count being taken after each rinsing. The count decreased with each washing, but gradually approached a value slightly above the monolayer equivalent. This led to the conclusion that a large portion of the acid was not attached to the surface as firmly as the monolayer film.

A series of similar runs was made on cadmium to see if the same thing happens. Cadmium also produces a fine powder when end-milled. Adsorption on end-milled cadmium also showed high results which were reduced by rinsing. Lathe-machined cadmium forms only a monolayer equivalent when exposed to the same acid concentration.

In order to eliminate the powder trouble, the zinc was lathe-machined with a cut-off tool. This gave swarf as continuous curls. The isotherms obtained indicate that slightly more than monolayer is adsorbed (Figure 9). This is probably due to adsorption in the radiating cracks on the surface or to a slightly low radiochemical standardization factor.

6. Adsorption on Vanadium

Adsorption isotherms (Figure 10) on end-milled vanadium show that this metal does not take up nonadecanoic acid easily. The adsorptive behavior resembles that of titanium. It was more difficult to obtain good reproducibility with vanadium than with most metals. This is probably because the surface was end-milled. In general, end-milled surfaces properties are harder to duplicate than lathe-machined ones.

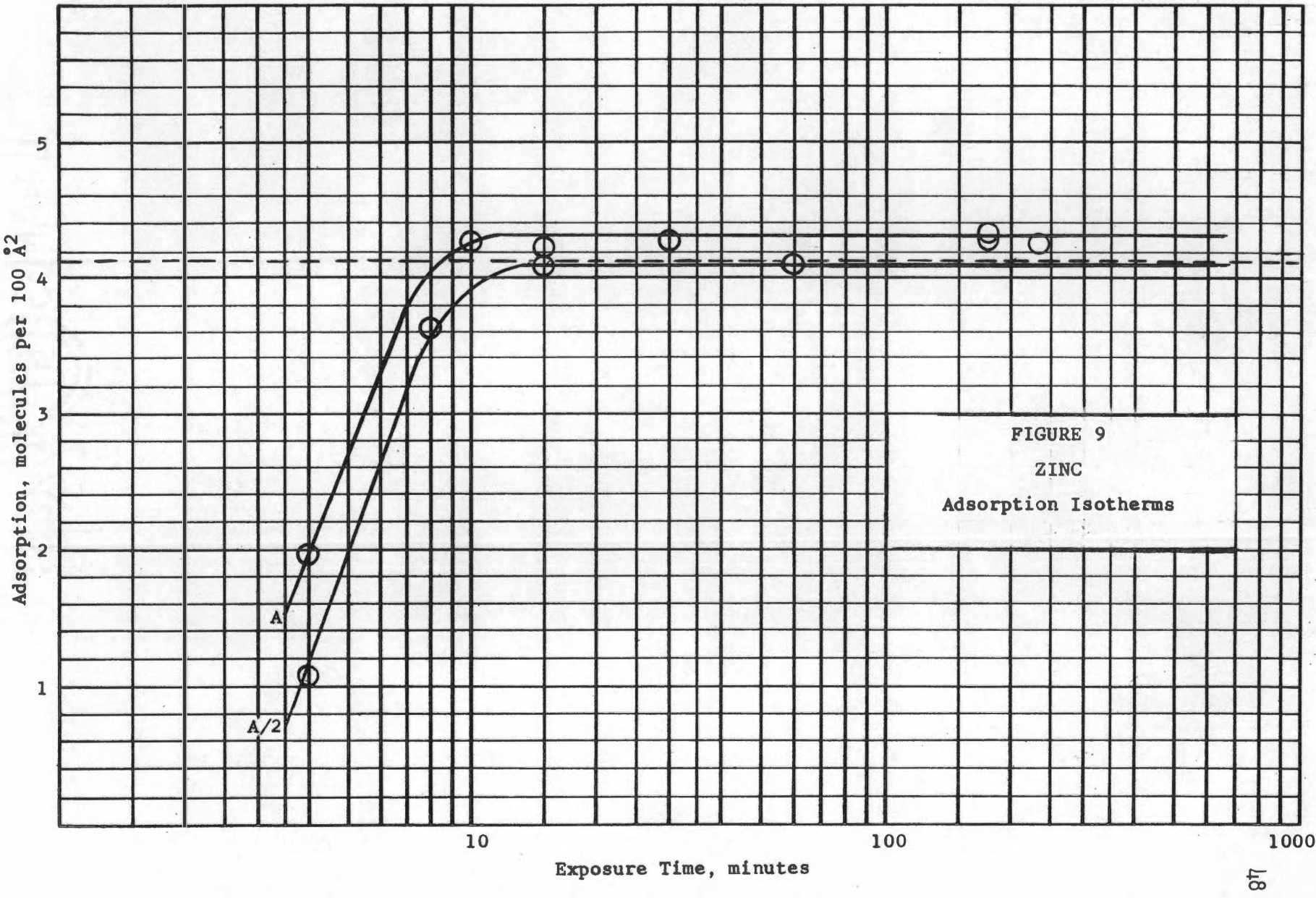


FIGURE 9

ZINC

Adsorption Isotherms

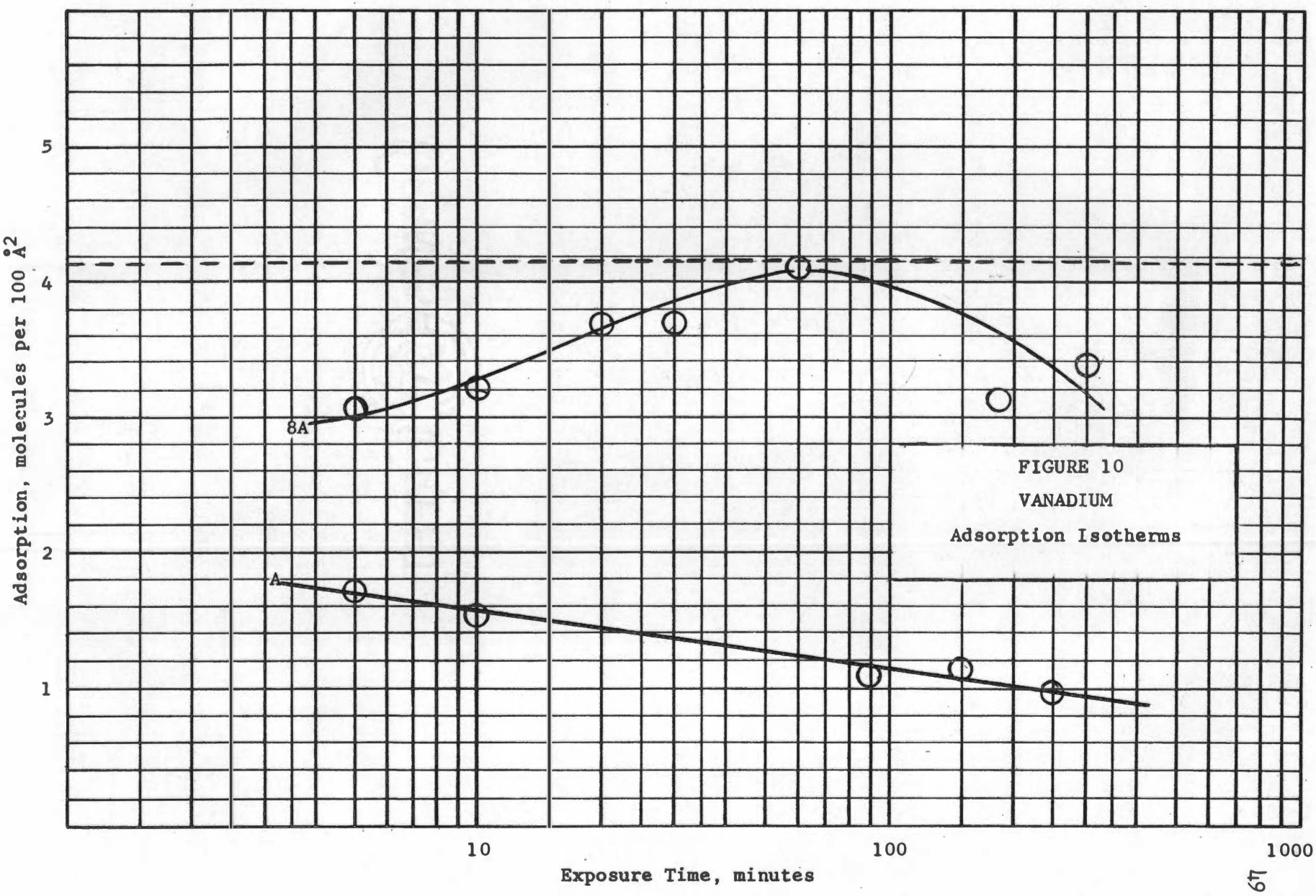


FIGURE 10

VANADIUM

Adsorption Isotherms

D. Radiochemical Exchange Rates

McGill[5] has established that once a monolayer is attained on many metals, a monolayer equivalent remains for long periods. For example, copper was found to have a full monolayer after seventy hours of exposure to "A" solution. Fort[6] found that when a sample which had been allowed to adsorb a monolayer of labeled acid was placed in an unlabeled acid solution, the sample lost part of its radioactivity. This indicated that the metal soap monolayer was not a static film but was continually undergoing a desorption and readsorption process. He also discovered that the rate of activity loss from a copper soap monolayer was independent of the concentration of the unlabeled solution as long as there was sufficient acid to replenish the monolayer.

Fort made exchange rate determinations on copper, magnesium, silver, and aluminum. The rates varied widely.

1. Quantitative Treatment

Consider an equilibrium exchange-producing reaction,

$$AX + SX^* = AX^* + SX \quad , \tag{1}$$

in which X^* represents the radioactive form of X. When the concentrations are designated as follows: $(AX) + (AX^*) = a$, $(SX) + (SX^*) = s$, $(AX^*) = x$, and $(SX^*) = y$, the rate of exchange is written,

$$\frac{dx}{dt} = R\,\frac{y}{s}\,\frac{a - x}{a} - R\,\frac{x}{a}\,\frac{s - y}{s} \quad . \tag{2}$$

Thus, the rate of formation of AX^* is given by the total rate of reaction between AX and SX regardless of labelling, R, times the fraction occurring between active SX molecules, $\frac{y}{s}$, and inactive AX molecules, $\frac{a - x}{a}$. The rate of destruction is obtained by multiplying R by the

fraction of the reaction in the reverse direction which occurs with labeled AX molecules, $\frac{x}{a}$, and inactive SX molecules, $\frac{s - y}{s}$. In the present study the observed change is:

Adsorbed Unlabeled Soap	+	Labeled Acid in Solution	→	Adsorbed Labeled Soap	+	Unlabeled Soap in Solution	+	Hydrogen

This reaction is irreversible so that the second term in equation (2) may be neglected, provided readsorption of the soap does not become important. The rate of radioactive pick-up then becomes,

$$\frac{dx}{dt} = R \frac{y}{s} \frac{a - x}{a} \quad , \tag{3}$$

where R is the rate of soap desorption.

The observed data are reported in terms of 0 to 100 per cent radioactive surface rather than the actual 0 to 1.44 per cent. In other words, the true fraction of radioactive surface is only 1.44 per cent of the reported labeled fraction; that is,

$$x = \frac{s}{y} X \quad ; \tag{4}$$

therefore,

$$\frac{dX}{dt} = R \frac{a - x}{a} \quad . \tag{5}$$

Fort found that the rate of desorption, R, could be found by measuring the amount of metal desorbed as soap by using microanalytical methods. The relation,

$$\text{Metal desorbed} = b \ln t + \text{constant}, \tag{6}$$

was found to hold for all metals studied. The rate of desorption reduced to the expression:

$$R = \frac{d[\text{metal desorbed}]}{dt} = \frac{b}{t} \quad . \tag{7}$$

Equation (5) now can be written,

$$\frac{dx}{dt} = \frac{b}{t}\frac{a - x}{a} \quad , \quad \text{or}$$

$$- \ln (a - x) = \frac{b}{a} \ln t + \text{constant} \quad . \qquad (8)$$

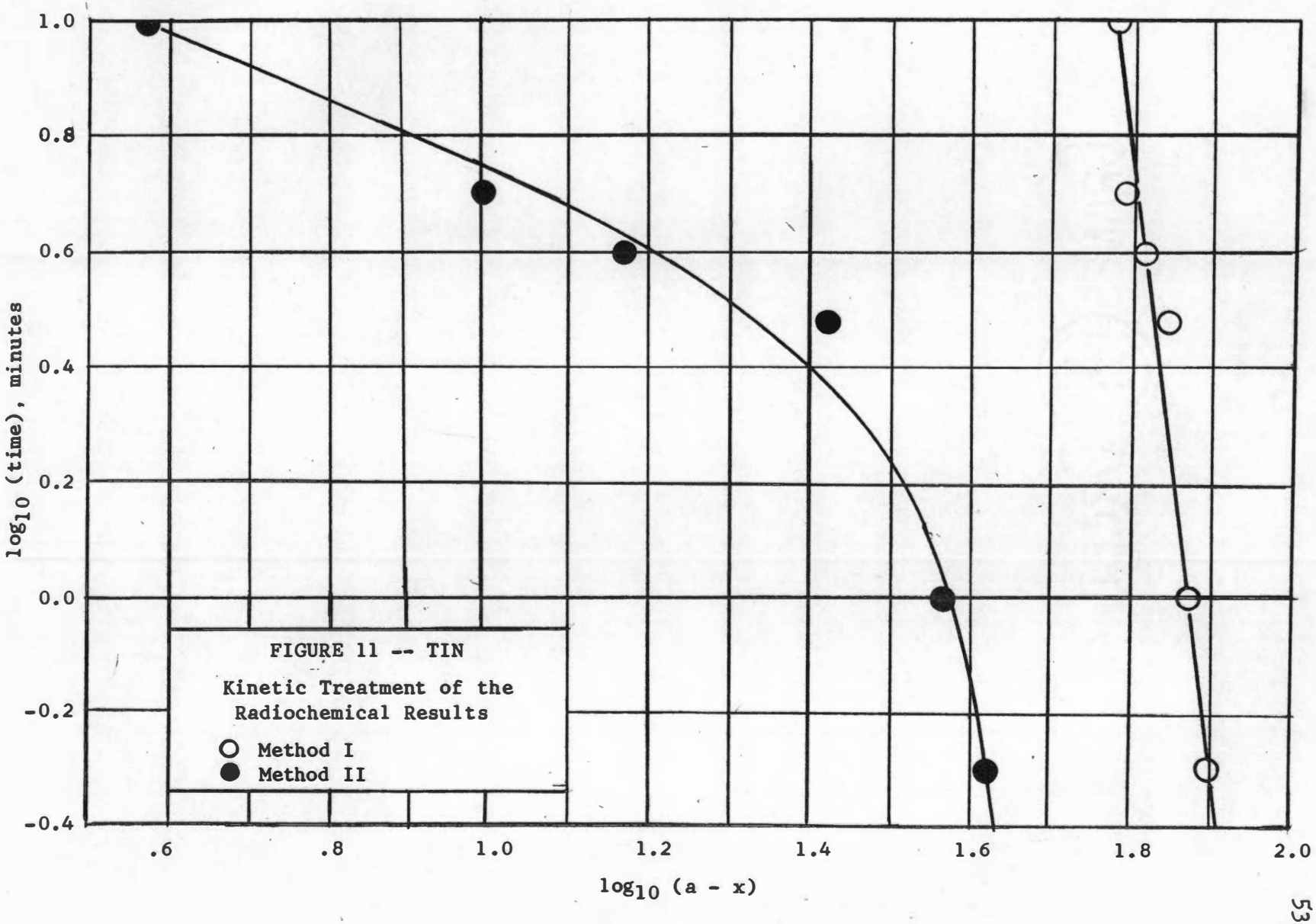
This is in agreement with Fort's experimental observation that a plot of log (exchange time) versus log (fraction of surface not covered by radioactive molecules) yields a straight line. From slopes of these lines, the value of b can be calculated, since,

$$b = a \cdot \text{slope} = 100 \cdot \text{slope} \quad .$$

2. Exchange Experiments

The procedure used to measure the rate of radioexchange was as follows. The sample was machined under unlabeled nonadecanoic solution, "U," and transferred to an adsorption cup of "U" for a total exposure time of fifteen minutes. Then the sample was transferred to another cup containing radioactive solution, "A." After varying exposure times to "A," the samples were removed, blotted with soft tissue, and counted.

a. Tin exchange. For the tin adsorption isotherms (Figure 5), it can be seen that tin never forms more than 41.8 per cent of a monolayer. It is difficult to apply the quantitative treatment described because the question arises as to whether $\frac{a - x}{a}$ should represent the fraction of the total surface that is not covered by labeled molecules or the fraction of the occupied area covered by unlabeled molecules. Both methods of treatment were tried, and the results are plotted in Figure 11.


1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
log10 (time), minutes
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
log10 (a - x)
FIGURE 11 -- TIN
Kinetic Treatment of the
Radiochemical Results
Method I
Method II

For method I, $\frac{a - x}{a}$ is defined as the fraction of the total area that is not covered by labeled molecules. This would include the 60 per cent of the area that is apparently not covered. This assumption yields a straight line plot whose slope gives a value of 8.95 for b. For method II, $\frac{a - x}{a}$ is defined as the fraction of the occupied surface that is not labeled. With this method, a non-linear curve is obtained. This leads to the conclusion that all of the tin surface is available for adsorption, although a monolayer is not attained.

b. Cadmium exchange. The standardized procedure for determining radioactive pick-up on cadmium presented no problem, since cadmium forms a monolayer. The slope from the straight line (Figure 12) obtained by plotting log exchange time versus log (a - x) gives a value of 2.6 for b.

c. Titanium exchange. The following data were obtained by the usual exchange method. After fifteen minutes exposure to "U" solution, the indicated counts were recorded.

"A" Exposure Time, min.	Counts/min.	Per Cent Monolayer
15	95	6.6
30	101	7.0
60	108	7.5
350	110	7.7

These data show that very little exchange occurs after fifteen minutes. This decay in the ability of the sample to exchange seems to parallel its loss in adsorptive capacity (Figure 6).

The standard exchange procedure has been to expose the sample to "U" for fifteen minutes, but it is apparent from the above data that

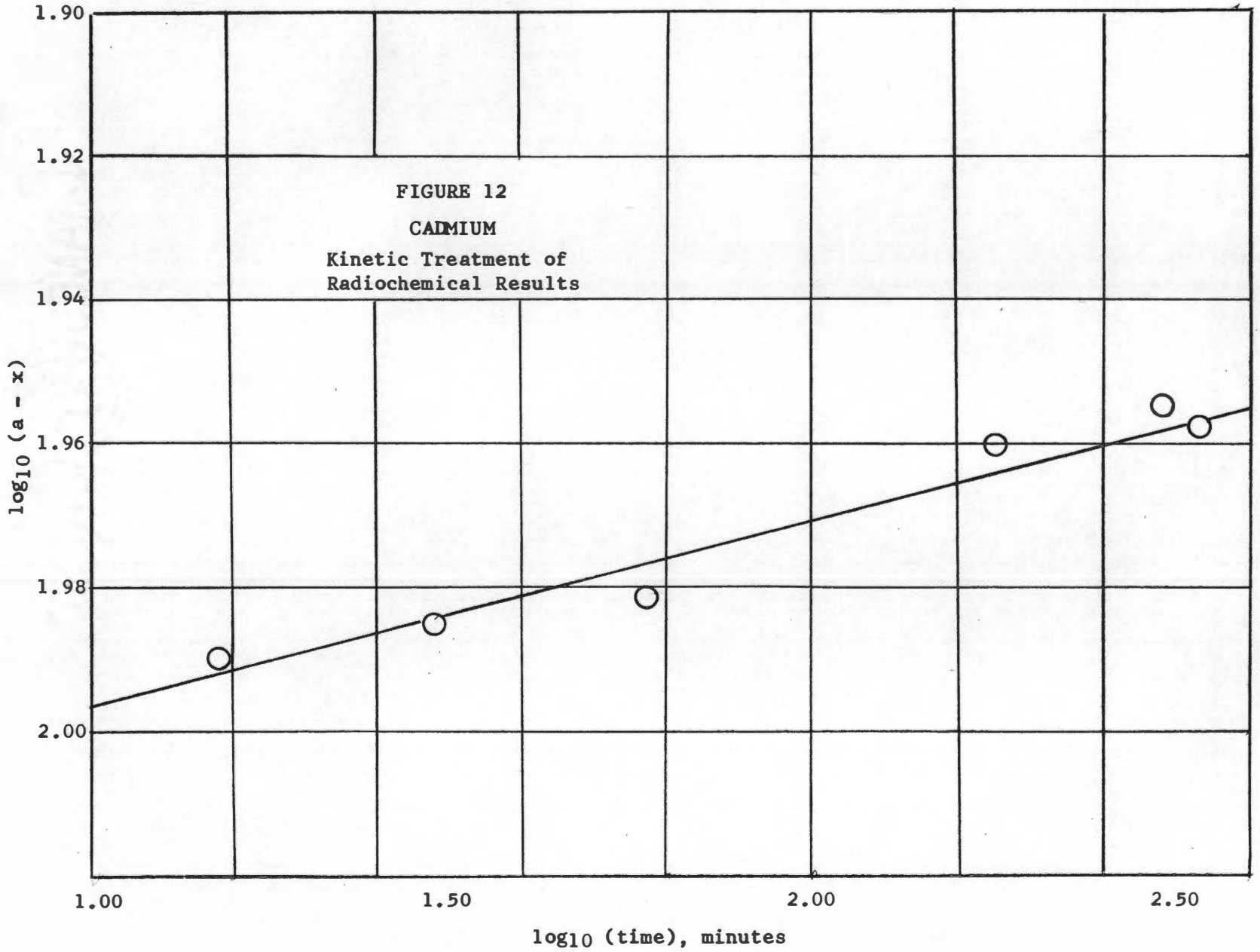


FIGURE 12

CADMIUM

Kinetic Treatment of
Radiochemical Results

much of the exchange capacity has decayed by this time. Accordingly, a new series of runs was made to illustrate the decay for the first fifteen minutes. The metal was machined under "U," transferred to a cup of "U" for varying times, then exposed to "A" for a standard time of fifteen minutes. The following data were observed:

"U" Exposure Time, min.	Counts/min.
1.5	131
3	114
15	95

This rapid decay prevents a total exchange of the partial monolayer (ca. 350 counts/min.). The difference in the exchange behavior of tin and titanium is striking. While neither attain more than about 40 per cent coverage, tin retains the ability to exchange its partial coverage rapidly and completely.

d. Zinc exchange. The results of the zinc exchange are plotted in Figure 13. Since zinc adsorbs a complete monolayer, the calculations were straightforward. A value of 6.31 was calculated for b.

e. Vanadium exchange. The exchange measurements on vanadium indicated that its behavior is similar to titanium. The results are slightly irregular. This is probably due to its rougher and less reproducible, end-milled surface. The following data illustrate the small extent of exchange:

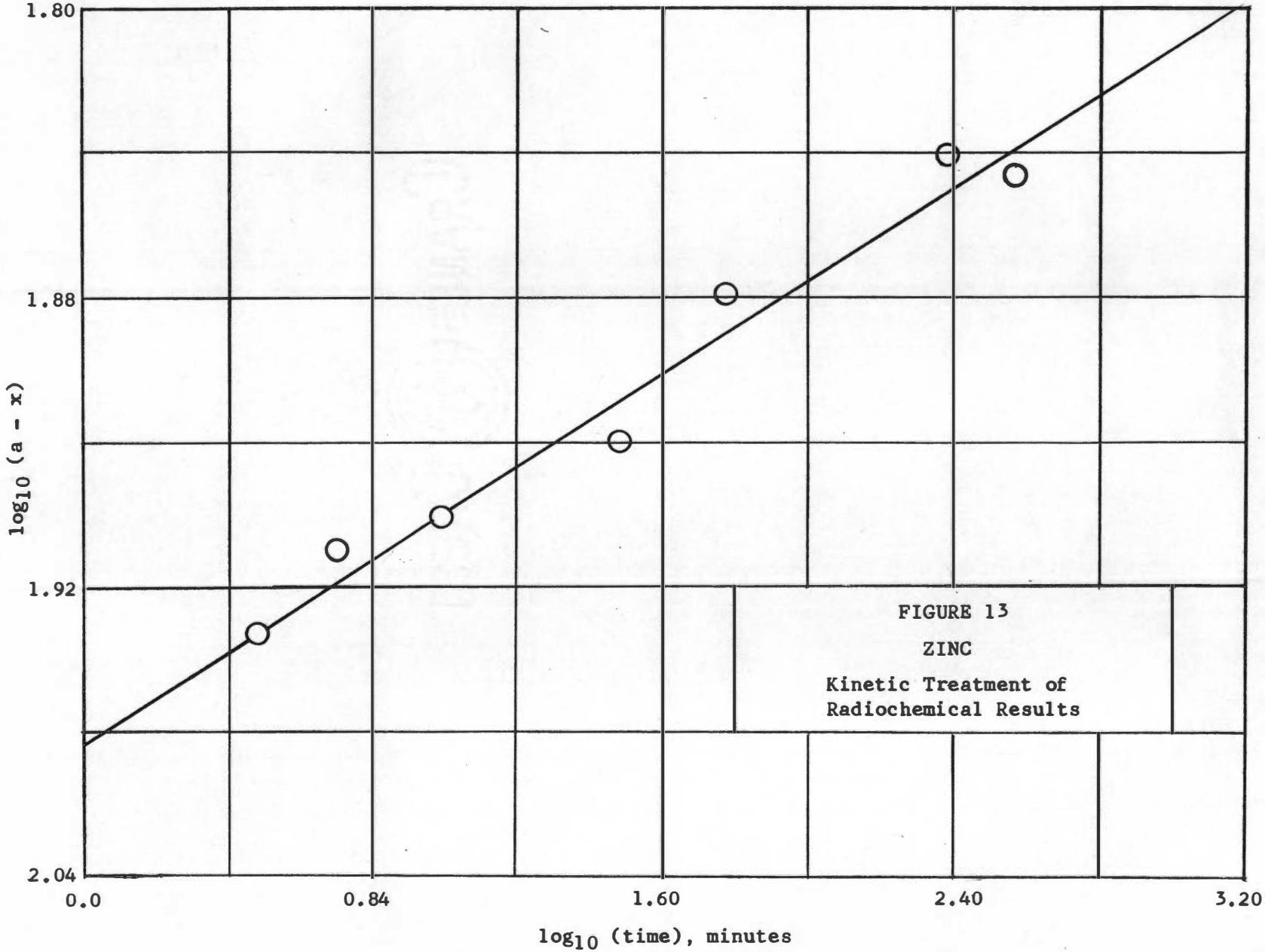


FIGURE 13

ZINC

Kinetic Treatment of
Radiochemical Results

"A" Exposure Time, min.	Counts/min.	Per Cent Monolayer
5	201	23.7
15	152	17.9
30	157	18.5
90	161	19.0
120	188	22.2
210	170	20.0
360	153	18.0

It is known from the adsorption isotherms that 300 counts/min. would be observed if immediate exchange occurred upon placing the sample in "A." Thus, it is evident that rapid exchange occurs at first but decays very quickly. The interpretation of these data is hindered by the low, erratic counts, but it is apparent that vanadium resembles titanium more closely than any other metal studied.

E. Soap Desorption Rates

Fort found from microanalytical techniques that each metal he studied followed the relation,

$$\text{Metal desorbed} = b \ln t + c \quad . \qquad (6)$$

He calculated the rate constants, b, for aluminum, copper, and silver, and found they decreased in that order. This is the same order observed from exchange data, but the values for b for a given metal were not the same by both methods. If the assumptions upon which equation (8) was derived are correct, b values should be the same in both types of experiment. However, a larger value was obtained from desorption

data for each metal. The interpretation of this will be discussed later.

1. Experimental Procedure

The standardized desorption experiments have been run as described by Fort so that the data found would be comparable to his. The sample was machined under "U" solution and transferred to a stirred cup of "U" for a total exposure time of fifteen minutes. The sample was then transferred to a fresh solution of "U" and exposed for varying time intervals. The sample was removed and the cyclohexane solution analyzed for its desorbed metal content. Very sensitive methods are required, since the quantities of metal are often less than one part per million. The details of the analytical methods are presented in Appendix II.

2. Results

The extreme sensitivity requirements and the nature of some of the investigated metals would not allow a determination of the desorption rate. For example, zinc and magnesium produced minute metal fragments during the machining process which would be carried through the analytical procedure to give theoretically impossible amounts of metal apparently desorbed.

a. Tin. When the desorption data for tin are plotted, the straight line shown in Figure 14 was obtained. The value of b was calculated from the slope of the line and found to be 743. These data establish that the acid is chemisorbed, a fact expected but not previously proved. The peculiar adsorption isotherm probably results from the high desorption which these data also confirm.

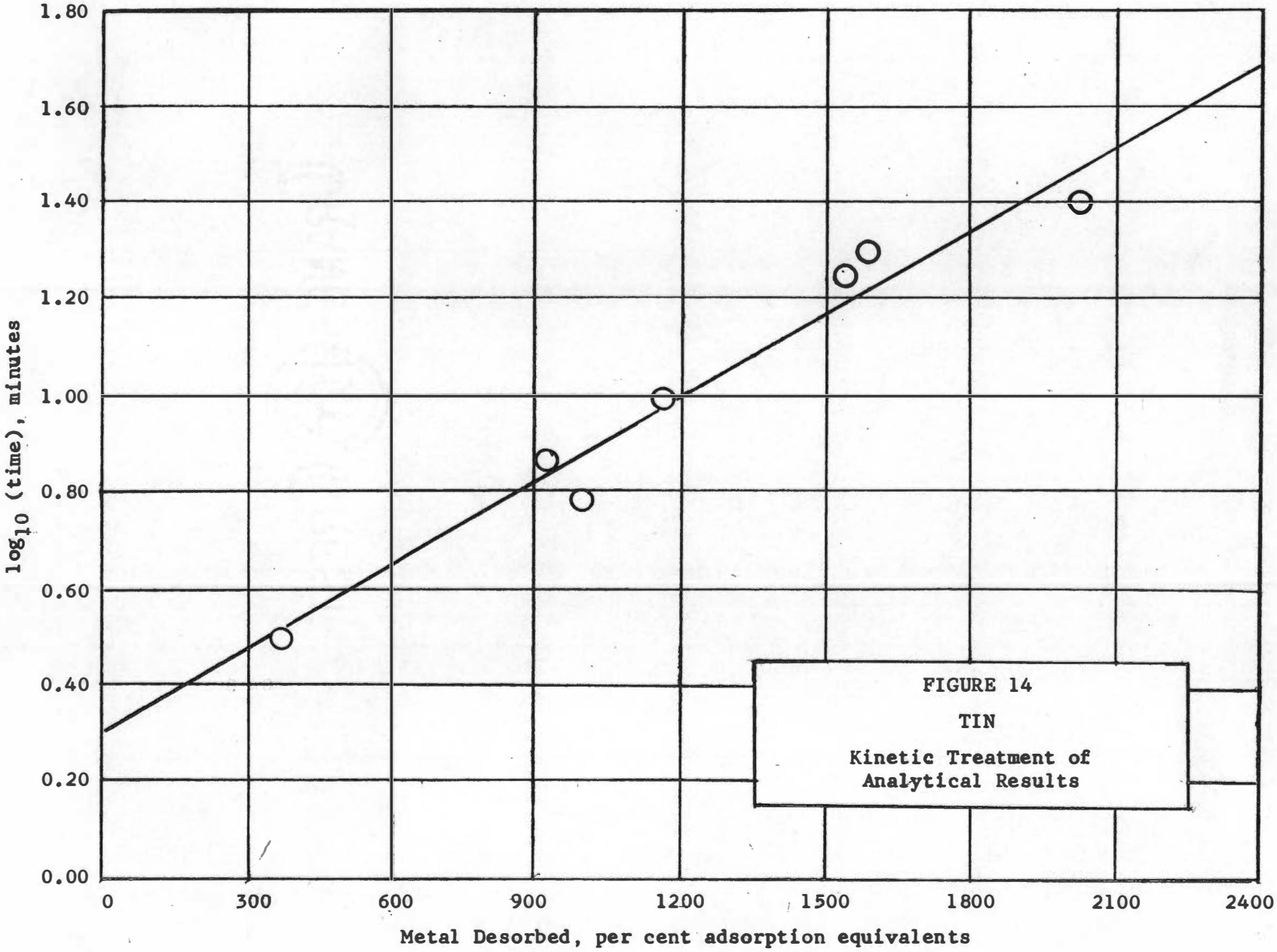


FIGURE 14

TIN

Kinetic Treatment of
Analytical Results

b. Titanium. Analyses of the desorbing solution failed to show the presence of any of the metal. The analytical method would fail to detect amounts less than about 0.1%, which would correspond to about 50 per cent of a monolayer if the titanium (II) soap were formed. This is roughly the amount adsorbed at the surface at any one time. Exposure times up to four hours were employed. These results strongly suggest the acid is physically adsorbed or, if not, the soap film is essentially static.

c. Vanadium. The analytical method used for vanadium indicated that there is no more than 0.3%, if any, of the metal in the desorbing solution. The same considerations applying to titanium are apparent here also.

d. Cadmium. Kinetic treatment of the analytical desorption data for cadmium yield a value of 254 for b. This was calculated from the plot in Figure 15.

F. Adsorption of n-Hexanoic Acid

1. The Possibility of Film Bridging

The adsorption studies of McGill, Fort, and this research indicate clearly that monolayers are formed on a number of metals. This means that either the metals must have unit roughness factors or the film must be able to bridge over surface breaches during formation. Zisman[10] has concluded from his work on oleophobic monolayers that films do not necessarily follow contours but may bridge depressions which are small compared to the cross-sectional area of the molecules. Bikerman[32]

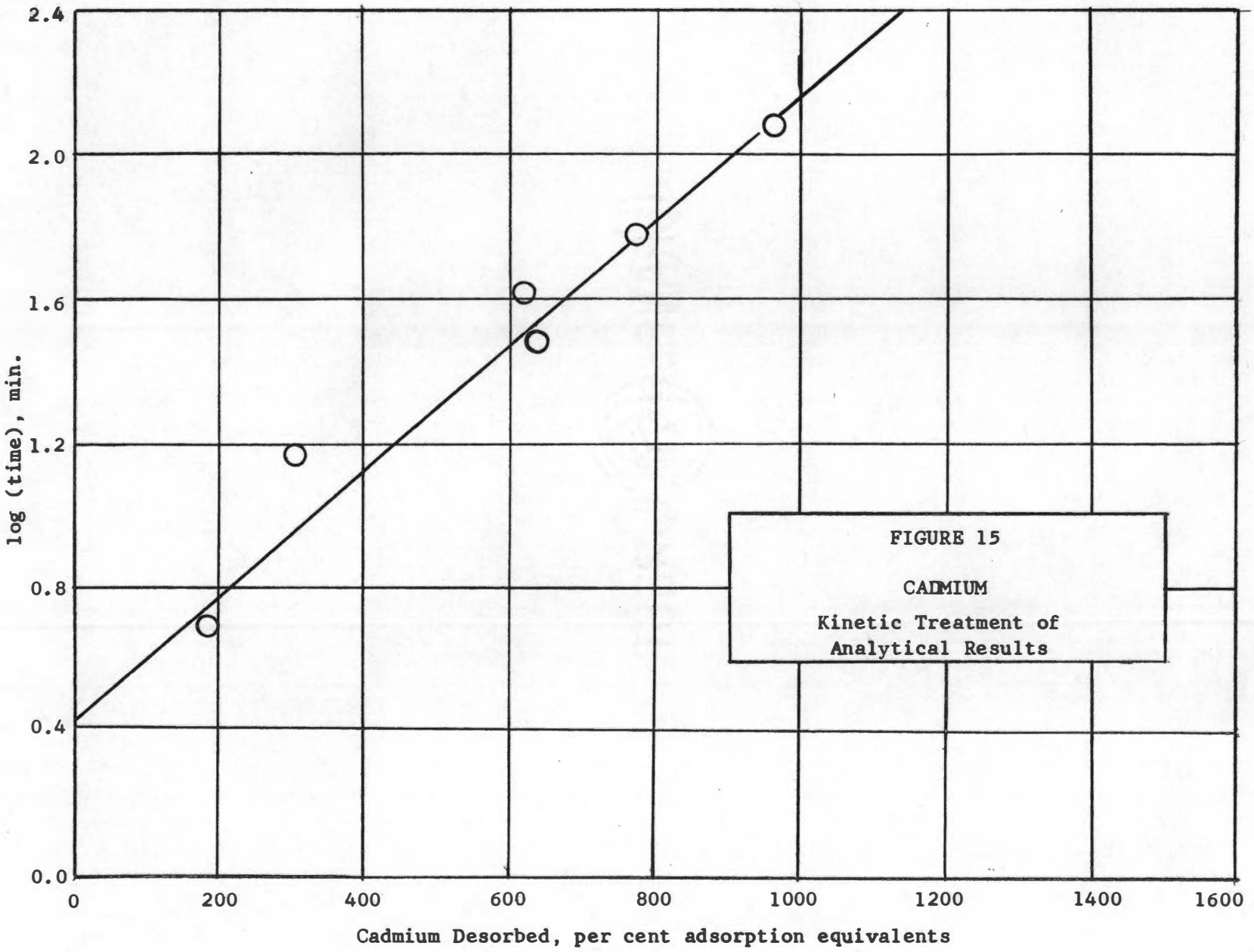


FIGURE 15

CADMIUM

Kinetic Treatment of
Analytical Results

has demonstrated that soap monolayers may be supported over much larger areas. When brass slides with 160 grooves incised 0.0019 cm. apart were dipped through barium stearate monolayers and withdrawn, the ratio of the area of the film on the water to that of the geometrical area of the slide was practically unity. Also, when a fine wire gauze was used, the area of the retracted film corresponded to the gauze area, not to that of the wires.

Arguments against bridging would be that Bikerman's films were already formed. The situation might be different while the films are forming. McGill[5] found that when a monolayer was desorbed, the amount of metal present corresponded to a monolayer of metallic soap. The questions arise as to how each molecule in a film can react if all of the molecules are not touching and why does the film not collapse during the exchange process.

2. Adsorption Experiments

In hopes of answering the problem, a series of adsorption measurements was made on a variety of metals, using n-hexanoic acid rather than n-nonadecanoic acid. The chain is short so that the van der Waal's forces present between the oriented long chain fatty acids will be much smaller in this film. It was expected that if the film were smooth only because of bridging, the hexanoic acid molecules would fall into the metal contours with resulting higher adsorption.

The metals were machined under "H" solution, which is the same molarity as "A" solution, and exposed to "H" solution for fifteen or thirty minutes. The results of these experiments are tabulated in

Table V, along with corresponding data with "A" solution. There is little difference in the amounts adsorbed on a given metal. This leads to the conclusion that bridging over areas much larger than the cross section of the carboxyl group is unimportant.

TABLE V

ADSORPTION OF HEXANOIC AND NONADECANOIC ACIDS

Metal	Exposure Time, min.	Hexanoic Acid	Nonadecanoic Acid
Copper	15	1348	1427
	30	1328	1490
Magnesium	15	1258	1379
	30	1041	1376
Cadmium	15	1680	1494
	30	1620	1602
Titanium	15	252	255
	30	267	343
Tin	15	301	397
	30	394	379

CHAPTER IV

DISCUSSION OF RESULTS

A. Factors Influencing Monolayer Formation

The various forms of the adsorption isotherm on different metals suggest that a number of factors affect the degree and ease of the adsorption process. Table VI lists the relative adsorption on all of the metals which have been investigated thus far. The metals are listed in the approximate order of the relative ease in formation of a monolayer. An absolute ranking is not possible, however. For example, silver does not attain more than 93 per cent of a monolayer, but the level of adsorption was observed by McGill to be attained fairly rapidly even from the most dilute solution (A/8). In contrast, aluminum does reach full coverage from the most concentrated solution, but not from the lower concentrations. An inspection of the table reveals that there is no immediately obvious relationship between the activity of the metal and the extent of coverage.

1. Thermodynamic Considerations

The energetic requirements of the reaction of metal with nonadecanoic acid have been considered by McGill. He and Fort have calculated the free energy change for the reaction,

$$HNd + \frac{1}{n} M \rightarrow \frac{1}{n} M(Nd)_n + \frac{1}{2} H_2 \quad , \qquad (9)$$

for a number of metals. The results of their calculations are presented in Table VII. The reaction of some metals which involve reactions

TABLE VI

RELATIVE ADSORPTION ON METALS

Metals which adsorb a monolayer easily
Magnesium
Lead
Nickel
Cobalt
Zinc
Cadmium
Copper
Metals which adsorb a monolayer or almost a monolayer with difficulty
Silver
Aluminum
Indium
Iron
Metals which do not adsorb a full monolayer
Tin
Vanadium
Titanium
Gold
Platinum

TABLE VII

FREE ENERGY CHANGE FOR SOAP FORMATION

Metal	$\triangle F$ (equation 9), kcal.
Co^{+2}	- 3.2
Fe^{+3}	+ 1.6
Pb^{+2}	+ 1.28
Cu^{+2}	+ 6.70
Ag^{+1}	+ 18.48

accompanied by positive free energy changes was explained by McGill to be due to the Kramer effect. The activation during machining furnished sufficient energy to promote the reaction of silver, but not the more noble metals such as gold and platinum. This is consistent with the fact that Kramer electrons have an energy of the order of one electron volt (23 kcal.).

2. High Desorption Rates

The difficulty with which the active metals, aluminum and indium, adsorb monolayers and the failure of tin to attain full coverage now appear to be due to their high desorption rates. On the other hand, vanadium and titanium have been shown to have essentially no desorption of their soaps. Their failure to adsorb a full monolayer is probably due to lack of reactivity.

3. Steric Factors

The extent of reaction of acid molecules with all of the metal atoms is unknown, but it is likely that with many of the metals the dinonadecanoate is formed. The formation of a trivalent soap would be sterically hindered. For example, aluminum (III) soaps have been prepared,[33,34] but the third acid molecule adds with difficulty. When the three chains are restricted to a hemisphere, as in the case of an absorbed molecule, the strain would be tremendous. McGill believed this was the reason aluminum attained monolayers with difficulty. There is the possibility that the aluminum (I) soap was formed, since some evidence for the existence of the +1 oxidation state has been obtained in liquid ammonia.[35]

On the basis of these considerations, all of the metals studied thus far may be divided into four groups:

Group a. These metals are the active ones whose rates of desorption are not large enough to prevent maintenance of full coverage. This group includes magnesium, cadmium, zinc, cobalt, and nickel.

Group b. This group includes those metals which would not react without the activation energy supplied by the Kramer effect. Copper, silver, and lead are in this category.

Group c. This group contains the active metals which do not attain monolayers or attain full coverage only from the more concentrated solutions. These metals, aluminum, indium, and tin, have such high desorption rates that a monolayer cannot be maintained.

Group d. Some of the metals do not react with the nonadecanoic acid and only partial monolayers are physically adsorbed. Gold and platinum belong to this group and probably vanadium and titanium also. The presence of the latter two metals is unexpected. They are probably not in this group for the same reason as the noble metals.

B. Comparison of Desorption and Exchange Rates

Fort has reported the values of the rate constant from the desorption equation (6) and the exchange equation (8) for a number of metals. His values, as well as those obtained in this research, are presented in Table VIII. These equations were derived with the assumptions that the surface was uniformly active and that the rate of desorption was the limiting factor in the exchange. The latter should be true, since a

TABLE VIII

RATE CONSTANTS

Metal	b (from desorption)	b (from exchange)	Ratio
Aluminum	929	18.7	49.7
Tin	743	8.95	88.2
Cadmium	253	2.6	97.3
Copper	76.4	22.8	3.4
Zinc	--	6.31	--
Magnesium	--	5.10	--
Silver	4	3.30	1.2

monolayer was present at all times during the exchange measurements. If these assumptions were correct, the values of b obtained from the two equations should agree for a given metal. However, the value of b from the desorption measurements has been greater with every metal studied than the value of b from the exchange measurements. The ratios of the two values are also given in Table VIII. The precision of the analytical determinations is not as good as that of the radiochemical measurements. However, the determinations are certainly not off as much as 97-fold.

Fort attributes the discrepancy between the b values to the fallacy of the assumption that the surface is uniform. He suggests that the metal surface contains "active spots" which, in a given time interval, adsorb and desorb faster than the surrounding sites. During this period, many molecules would be desorbed, but the radioactive exchange would amount to only one molecule.

Another explanation is available if the monolayer exists in clusters, or islands, as proposed by Epstein.[16] If these "sheaves" of molecules exist, a desorbing molecule in the center of the cluster would have a much greater potential barrier to overcome than one around the periphery of the cluster. Greater desorption and readsorption, then, would be expected around these edges of the clusters. This would explain the differences in the b values. If this were the true and only cause of the discrepancy, the relative size of the islands on different metals would be reflected in the rate ratios. Thus, it might be assumed that the monolayer on silver is barely broken into clusters, whereas the ones on tin, aluminum, and cadmium are divided into many smaller islands. These conclusions are not justified, however, because the discrepancy

might be due totally, or in part, to other causes such as "active sites" or adsorption at only the high points of a rough surface.

C. Surface Roughness

The fact that monolayers are formed whose areas are the same as the apparent geometrical area of the sample implies that essentially smooth metal surfaces were produced by machining. This was not expected, since most metal polishing techniques give surfaces which have roughness factors considerably greater than unity. The possibility of the film bridging over gaps on the metal surface seemed to be a more acceptable explanation. However, the smooth surface is consistent with the fact that McGill observed a monolayer equivalent of metal was carried into solution when the monolayer film was desorbed. In other words, every molecule in the film appeared to be a soap molecule. If portions of the film were not in contact with metal, it is not likely that all of the molecules would be soap molecules. Nevertheless, there is the possibility that the acid molecules desorbed, readsorbed, and reacted to form soaps during the desorption period.

The failure of n-hexanoic acid to adsorb to a greater extent than n-nonadecanoic acid is evidence that bridging has not occurred over areas much larger than the area of the carboxyl group (25 $Å^2$). It is concluded, therefore, that the majority of the metal surface is smooth down to the order of about 25 $Å^2$. This conclusion is supported by the electron photomicrographs and diffraction patterns which are discussed in Appendix V.

D. Suggestions for Additional Work

The metal surfaces obtained in these studies are unusual, and the results obtained on the clean, activated surfaces are often not comparable to those obtained from other studies. This makes further investigations desirable and necessary to obtain a complete understanding of the adsorption process.

One of the areas which has been virtually untouched is adsorption on alloys. The adsorption characteristics of some mixtures would be most interesting. For example, the behavior of alloys of tin and lead would be of interest, since the former adsorbs very little, while the latter forms a monolayer rapidly. Investigation of alloys should be accompanied, if possible, by a determination of the surface content, since this might be altered from the bulk content during the machining process.

The use of other solvents might be valuable. Thus far, only cyclohexane has been used extensively. The possibility of mixed monolayer formation should be investigated. Many cutting oils and lubricants employ hydrocarbons as diluents. A knowledge of the extent to which these solvents are incorporated into the adsorbed film would be worthwhile.

During the course of this research, all machining techniques have been standardized as much as possible to prevent a possible variation in the degree of activation of the metal. However, a study of the variation in the Kramer effect with varying cutting speeds and other straining methods would be of considerable interest.

CHAPTER V

SUMMARY

A study has been made of the adsorption of n-nonadecanoic acid on freshly machined metal surfaces. This is an extension of the work of Smith and Allen,[4] McGill,[5] and Fort.[6] The machining techniques employed were the same as used by these workers and have been shown to produce an activated surface. Adsorption on solution-machined cadmium and zinc reached saturation levels which corresponded to monolayers, if unit roughness were assumed. Tin did not attain full monolayer coverage. Desorption rate experiments on this metal show that the acid reacts to form the metallic soap which was rapidly desorbed into solution. As a result of this rapid desorption, complete coverage was not attained. Radiochemical exchange occurred in a pattern which would be expected if the entire surface were available for adsorption, not just that which was actually covered.

Titanium and vanadium also fail to adsorb full monolayers. However, in contrast to tin, desorption measurements fail to indicate the presence of detectable quantities of the metals in desorbing solutions. This indicated that the fraction of a monolayer on the surface was physically adsorbed. However, since the radiochemical exchange results showed that very little exchange occurred, there is the possibility that the adsorbed material was an essentially static chemisorbed partial monolayer.

The rates at which the metallic soaps desorb in n-nonadecanoic acid solutions have been investigated for tin, cadmium, titanium, and

vanadium. Radiochemical exchange of unlabeled molecules in the adsorbed films for labeled ones has been determined for these metals and also zinc. In each case where it was possible to calculate the rate constants for both processes, the rate of desorption was found to be faster than would have been predicted from the rate of exchange. This has been observed previously by Fort[6] and was apparently due to the fact that the surface was not homogeneous, but certain portions or centers are more active than others.

Adsorption data of n-hexanoic acid, under the same conditions as employed with n-nonadecanoic acid, show that there is very little difference on a molar basis in the extent of adsorption with the two acids. This means that there was very little bridging over breaches on the surface which were much greater than the cross-sectional area of the carboxyl group. If this had occurred to a large extent with nonadecanoic acid, the short chain hexanoic acid would have fallen into these gaps, with higher adsorption resulting. This conclusion that the surface is relatively smooth is supported by evidence from electron photomicrographs and electron diffraction experiments.

APPENDIXES

APPENDIX I

PREPARATION OF CARBON-14 LABELED NONADECANOIC ACID

Labeled n-nonadecanoic acid was synthesized by a Grignard reaction. The method is the same as used by Allen,[4] which was a modification of the procedure and apparatus of Dauben, Reid, and Yankwich.[36] The following reactions were involved in the synthesis:

$$C_{18}H_{37}Br + Mg \rightarrow C_{18}H_{37}MgBr$$

$$H_2SO_4 + BaC^*O_3 \rightarrow BaSO_4 + H_2O + C^*O_2$$

$$C_{18}H_{37}MgBr + C^*O_2 \rightarrow C_{18}H_{37}C^*O_2MgBr$$

$$C_{18}H_{37}C^*O_2MgBr + HCl \rightarrow C_{18}H_{37}C^*O_2H + MgBrCl$$

A. Grignard Reagent

Octadecyl bromide which had been prepared and purified by Fort[6] was employed in preparing the Grignard reagent. A 50-ml. graduated cylinder was used as the reaction vessel. The top of the cylinder was fitted with a "T" tube so that a dry nitrogen stream could be passed over the solution. A small glass-enclosed magnetic stirrer was placed in the bottom of the cylinder. About 2.25 g. of the bromide was dissolved in 30 ml. of anhydrous ether which had been dried and stored over sodium. Approximately 0.14 g. of freshly machined magnesium turnings was added to the solution in the cylinder, and a small crystal of iodine introduced. The solution was warmed to start the reaction. The yellow color of the iodine soon disappeared, but the reaction proceeded slowly. From five to ten hours was usually required for complete

reaction. Once the reaction started, the cylinder was glass-stoppered and sealed with wax until ready for use. On cold days the Grignard reagent precipitated from the ether.

B. Carboxylation

Due to the expense of the carbon-14 preparation and the small working quantities, several "cold" runs were made with unlabeled barium carbonate. Thus, familiarization with the apparatus and practice in developing the small quantity of product was obtained. The carboxylation apparatus is shown in Figure 16. One millimole (198.4 mg.) of dry barium carbonate was placed in the generating flask and distributed over the bottom by swirling the flask. Five milliliters of concentrated sulfuric acid was pipetted into the acid burette, and the entire system assembled. The apparatus was evacuated and tested for leaks. The system was filled with nitrogen and evacuated three times. When atmospheric pressure was reached after the third flushing, the plug was removed and nitrogen was allowed to pass through the system. With a Mohr pipette, 10 ml. of octadecylmagnesium bromide was removed from the graduated cylinder and introduced into the reaction flask. The volume was increased to 50 ml. by adding dry ether to the flask; then the plug was replaced.

The nitrogen atmosphere was reduced to slightly less than atmosphere pressure; then the contents of the reaction flask were frozen by immersing the flask in a Dewar flask of liquid nitrogen. When the solution was completely frozen, the system was evacuated. In order to remove the dissolved nitrogen in the frozen ether, the solution was

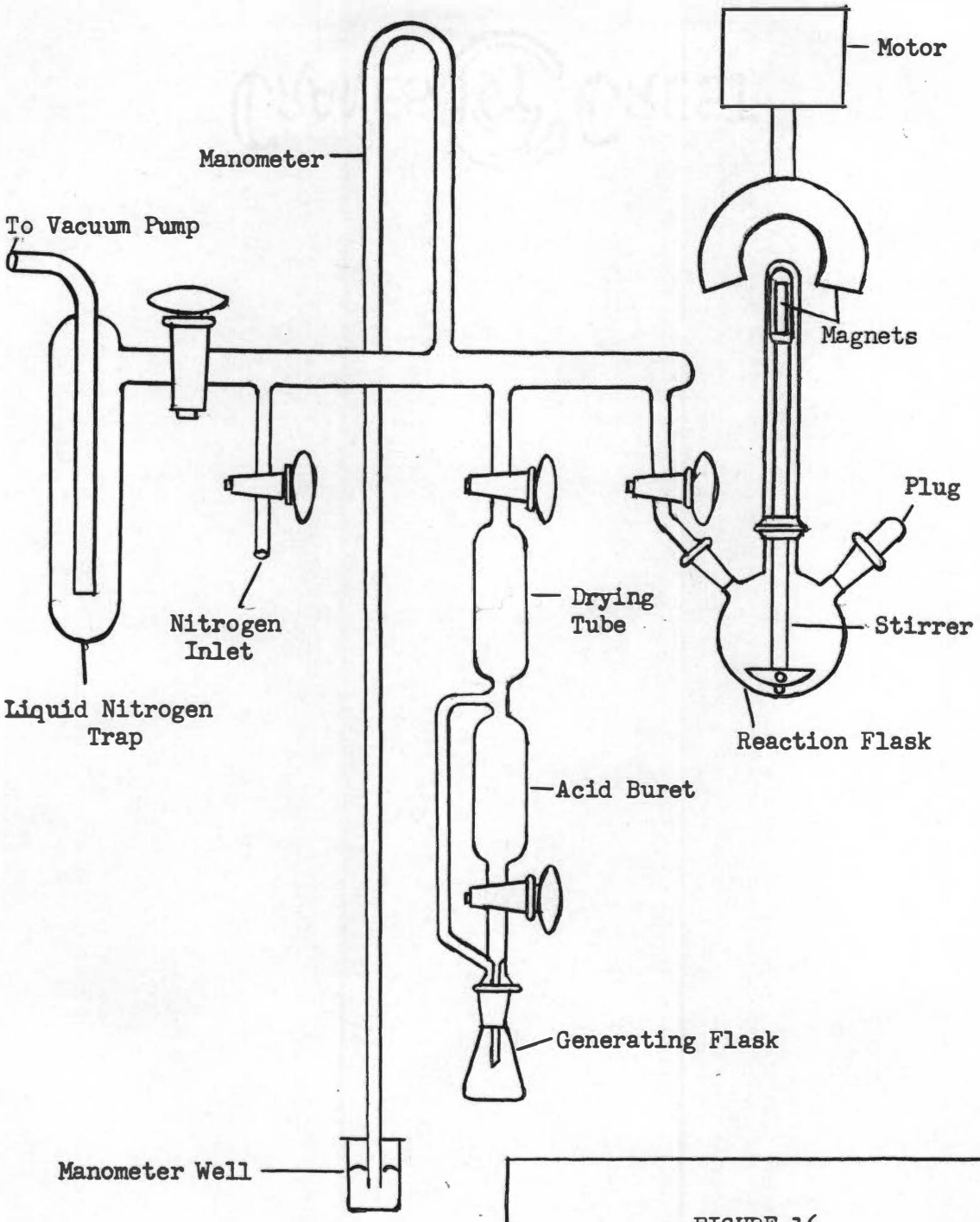


FIGURE 16

CARBOXYLATION APPARATUS

alternately melted and refrozen. The solution was melted by replacing the Dewar flask of liquid nitrogen with one containing acetone which was lowered to about -20° with "Dry Ice." After melting occurred, the nitrogen was liberated and removed by evacuation after the ether was refrozen. Usually two or three of these cycles were required before no further gas was evolved.

When the nitrogen had been removed and the solution melted, the magnetic stirrer was started. Generation of the carbon dioxide gas was begun by adding the sulfuric acid slowly to the barium carbonate flask. After all the acid had been admitted, the flask was heated gently with a low flame to drive off the last trace of carbon dioxide.

The stirrer was stopped and the reaction flask contents were frozen when the manometer indicated that gas generation and absorption by the Grignard reagent was complete. The system was then fully evacuated. The reaction flask was isolated from the remainder of the system and the solution melted at -20°. After fifteen minutes of vigorous stirring, the flask was opened to the system and filled with nitrogen. The flask was then removed and the reaction product treated as indicated subsequently.

C. Product Treatment

The contents of the reaction flask were transferred to a 500-ml. separatory funnel. The reaction flask was rinsed with ether, 10 per cent hydrochloric acid solution, then again with ether. These rinsings were added to the separatory funnel. The solution was hydrolyzed with

four portions of 10 per cent hydrochloric acid. The ether layer contained the nonadecanoic acid and the hydrolyzed product of the surplus Grignard reagent. The ether solution was suspended in 10 per cent sodium hydroxide solution. The aqueous layer was removed and extracted three times with ether to remove the octadecane formed by hydrolysis of the excess Grignard reagent. The aqueous layer was then acidified with 10 per cent hydrochloric acid, and the liberated n-nonadecanoic acid extracted with several portions of ether. These combined ether extracts were evaporated to dryness. The acid was recrystallized from acetone.

For the labeled run, 30.4 mg. of 10.6 per cent labeled barium carbonate was obtained from the Atomic Energy Commission at Oak Ridge. This material, containing one millicurie of activity, was diluted with unlabeled barium carbonate to a total weight of 198.4 mg. For the labeled reaction, a 55 per cent yield of purified product was obtained, with a melting point of 67.0-67.5°.

D. Unlabeled Acid

For each of the runs a fresh Grignard reagent solution was prepared, but only about a third of each was used. These unused portions were combined to make a large quantity of unlabeled acid. The Grignard reagent was poured into a 500-ml. beaker which was about one-fourth full of a "Dry Ice"-ether slurry. The slurry was stirred until all of the "Dry Ice" sublimed, then it was hydrolyzed with a 10 per cent hydrochloric acid solution. The product was purified in the same manner as described above.

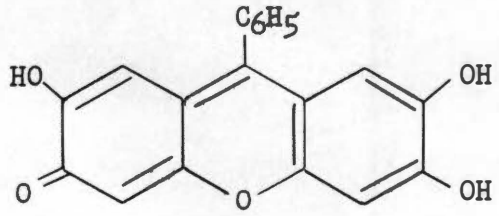
APPENDIX II

MICROANALYTICAL METHODS

A. Tin

1. Analytical Method[37]

The tin desorption experiments required a method for the analysis of tin in the concentration range of 0.01 p.p.m. With a few modifications, a method developed by Luke[38] has been found to be satisfactory. Phenylfluorone (2,6,7-trihydroxy-9-phenylisoxanthene-3-one) is used as a spot test for germanium.[39] The interference of tin suggested its use as a reagent for the photometric determination of tin, which application was developed by Luke. The reagent produces a pink coloration with tin (IV), but the exact nature of the product is unknown. Feigl[39] suggests the possibility of ester formation with the phenolic groups (II) or the production of an adsorption compound between $SnO_2 \cdot aq.$ and (I) with the $=C(OH)CO$ group participating.



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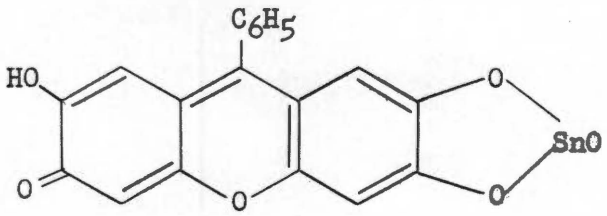


II

The following solutions were prepared.

a. Reagent solutions. A stock solution of reagent was prepared by dissolving 0.0500 g. of phenylfluorone in 50 ml. of methanol and

1 ml. of hydrochloric acid, then diluting to the mark with methanol. For use in the determinations, a secondary solution was prepared by diluting 25 ml. of the stock solution to 250 ml.

b. Standard solutions. The primary tin standard was prepared by dissolving 0.2500 g. of pure tin metal with 10 ml. of sulfuric acid in a 250-ml. volumetric flask. Then 30 ml. of sulfuric acid was added. Dilution with deionized water to the mark after the solution had cooled yielded a standard containing 1 mg./ml. A stock solution of 1 part concentrated hydrochloric acid to 9 parts water was prepared. This (1:9) hydrochloric acid solution was used in all standard dilutions and unknown preparations. Distilled water, passed through a 4-ft., 25-mm. diameter column packed with Amberlite MB-3 ion exchange resin, was used in all aqueous reagents. A secondary tin standard was prepared by diluting 2.00 ml. of the primary standard to a final volume of 250 ml. with (1:9) hydrochloric acid. By diluting 5.00 ml. of the secondary standard to a final volume of 100 ml., a tertiary standard containing 0.4 µg/ml. was obtained.

c. Buffer solution. A pH buffer solution was prepared by dissolving 450 g. of hydrated sodium acetate in about 350 ml. of water. The solution was heated, filtered, and transferred to a 1-liter volumetric flask. It was cooled and diluted to the mark.

2. Procedure

A procedure similar to Luke's was used; however, it was found necessary to destroy the excess hydrogen peroxide which was added to oxidize the tin. Also it was found unnecessary to add a gum arabic solution at the concentration range studied.

Calibrating solutions, ranging from 0 to 6 micrograms per 25 ml. of solution, were prepared in the following manner. The appropriate amounts of tertiary standard were transferred with Mohr pipettes to 25-ml. Pyrex graduated cylinders. Then 1 ml. of 3 per cent hydrogen peroxide was introduced into each cylinder. The cylinders were placed on a hot plate and heated for about forty-five minutes until the volume was reduced to about 4-5 ml. This procedure destroys the excess hydrogen peroxide which, if not removed, was found to give erratic results, apparently due to the oxidation of the phenylfluorone. Luke does not report this difficulty.

After the cylinders had cooled, 5 ml. of buffer solution was added and the solution diluted to about 19.5 ml. with deionized water. The pH of the solutions was then adjusted to 3.5 with a 4N sulfuric acid solution and Accutint indicator paper Nos. 50 and 60. The volume was diluted to 20 ml., and 5 ml. of phenylfluorone reagent added. With a Beckman model DU spectrophotometer, the optical densities at 510 mμ were determined. Measurements were made ten minutes after the addition of the phenylfluorone, since fading was observed after prolonged standing. The calibration curve is shown in Figure 17.

The tin from the soap desorption experiments was brought into an aqueous phase by extracting the cyclohexane solution twice with 5-ml. portions of (1:9) hydrochloric acid. After the addition of 1 ml. of 3 per cent hydrogen peroxide, the unknowns were treated in an identical manner to that used for the calibrating solution.

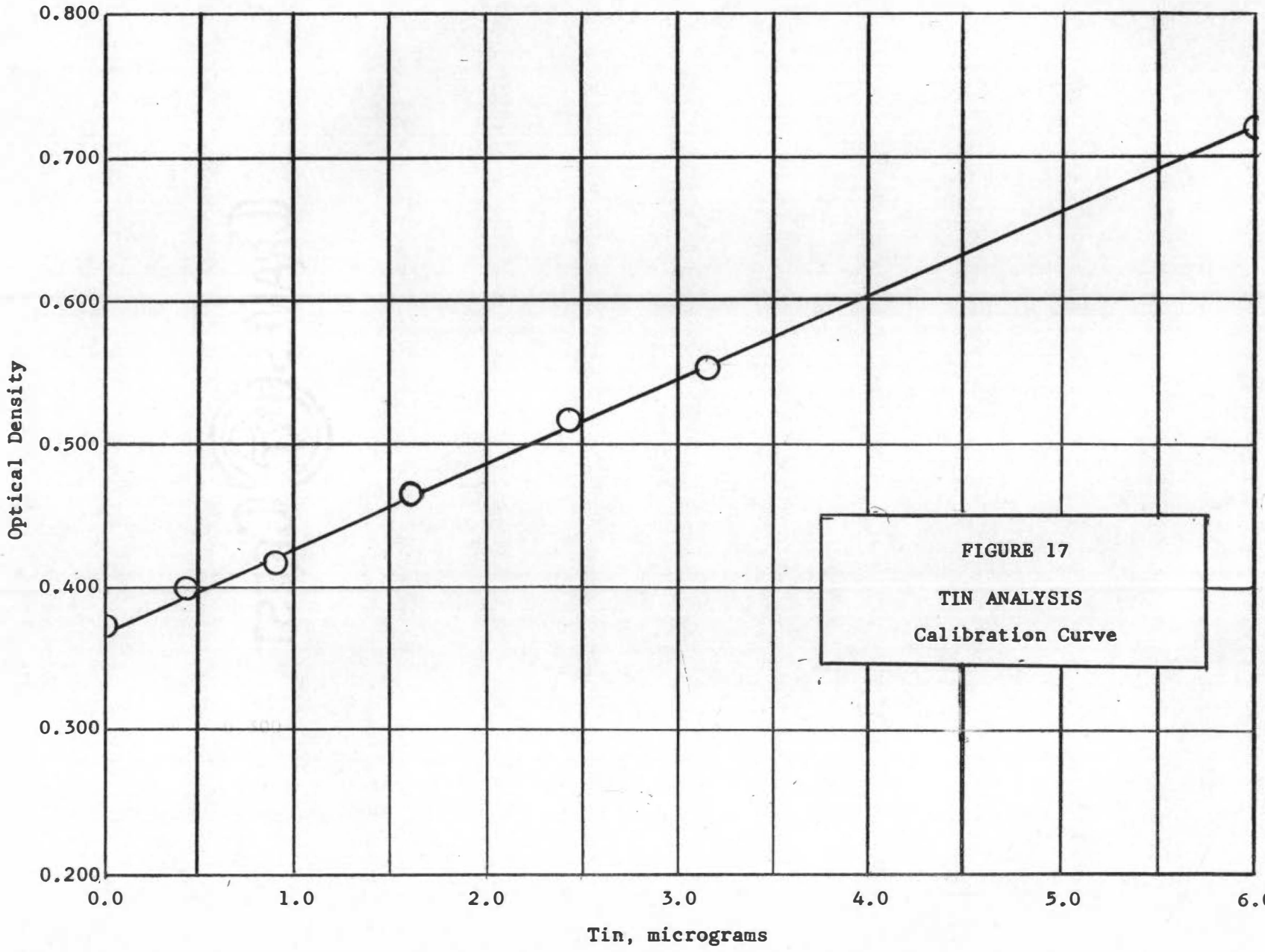


FIGURE 17

TIN ANALYSIS

Calibration Curve

B. Titanium

1. Analytical Method

In order to determine the rate at which titanium soap was desorbed into solution, it was necessary to find a suitable analytical method for titanium. The most promising one was that of Yoe and Armstrong.[40] The reagent used, disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron), forms a yellow complex with titanium and blue-purple complexes with iron.

The following reagents were used:

a. Buffer solution. A pH 5 buffer solution was prepared by dissolving 450 g. of hydrated sodium acetate in 350 ml. of water. The solution was heated, filtered, and transferred to a 1-liter volumetric flask containing 240 ml. of acetic acid. After cooling, the solution was diluted to the mark.

b. Reagent solution. A solution of 4 g. of Tiron in 100 ml. of deionized water was prepared.

c. Standard titanium solutions. A primary standard solution in 0.5 M. sulfuric acid was prepared by dissolving 0.2500 g. of pure titanium with 6.8 ml. of concentrated sulfuric acid and diluting to the mark in a 250-ml. volumetric flask. A secondary solution was made by diluting 2.00 ml. of the primary standard with 0.5 M. sulfuric acid to 250 ml. By diluting 5.00 ml. of the secondary standard with 0.5 M. sulfuric acid to 100 ml., a tertiary standard containing 0.40γ/ml. was obtained.

2. Procedure

Calibration solutions were prepared by adding 10 ml. of buffer, the appropriate amount of standard, and then 0.25 ml. of 3 per cent hydrogen peroxide to a 25-ml. graduated cylinder. The solution was then diluted to 23 ml. with 0.5 M. sulfuric acid. After the addition of 2.00 ml. of Tiron reagent, the optical density was determined against a blank.

Desorption measurements were made by machining the sample under "U" solution, exposing it to a stirred "U" solution for fifteen minutes, then transferring the sample to stirred "U" cups for varying lengths of time. The titanium was extracted from the cyclohexane with three 4-ml. portions of 0.5 M. sulfuric acid. These samples were treated identically to the calibration solutions. Originally only titanium was determined at its absorption maximum, 380 mμ. It was found, however, that a slight absorption peak was occurring at 560 mμ which corresponds to that of the iron complex. The source of the iron was not known; nevertheless, attempts were made to determine the amounts of titanium and iron present. The method of Yoe and Armstrong where dithionite is added after the iron has been determined did not work, due to precipitation of sulfur and subsequent fading of the solution. The method of Szarvas and Csiszar,[41] which uses ethylene diamine tetraacetate to mask the iron, was tried. However, the titanium complex was destroyed, as well as the iron, at the small concentration range used. Since iron and titanium absorb at 400 mμ, but only iron at its peak, 560 mμ, it was possible to measure the absorbance at these two wavelengths and thus determine both metals. Figure 18 shows the calibration curves.

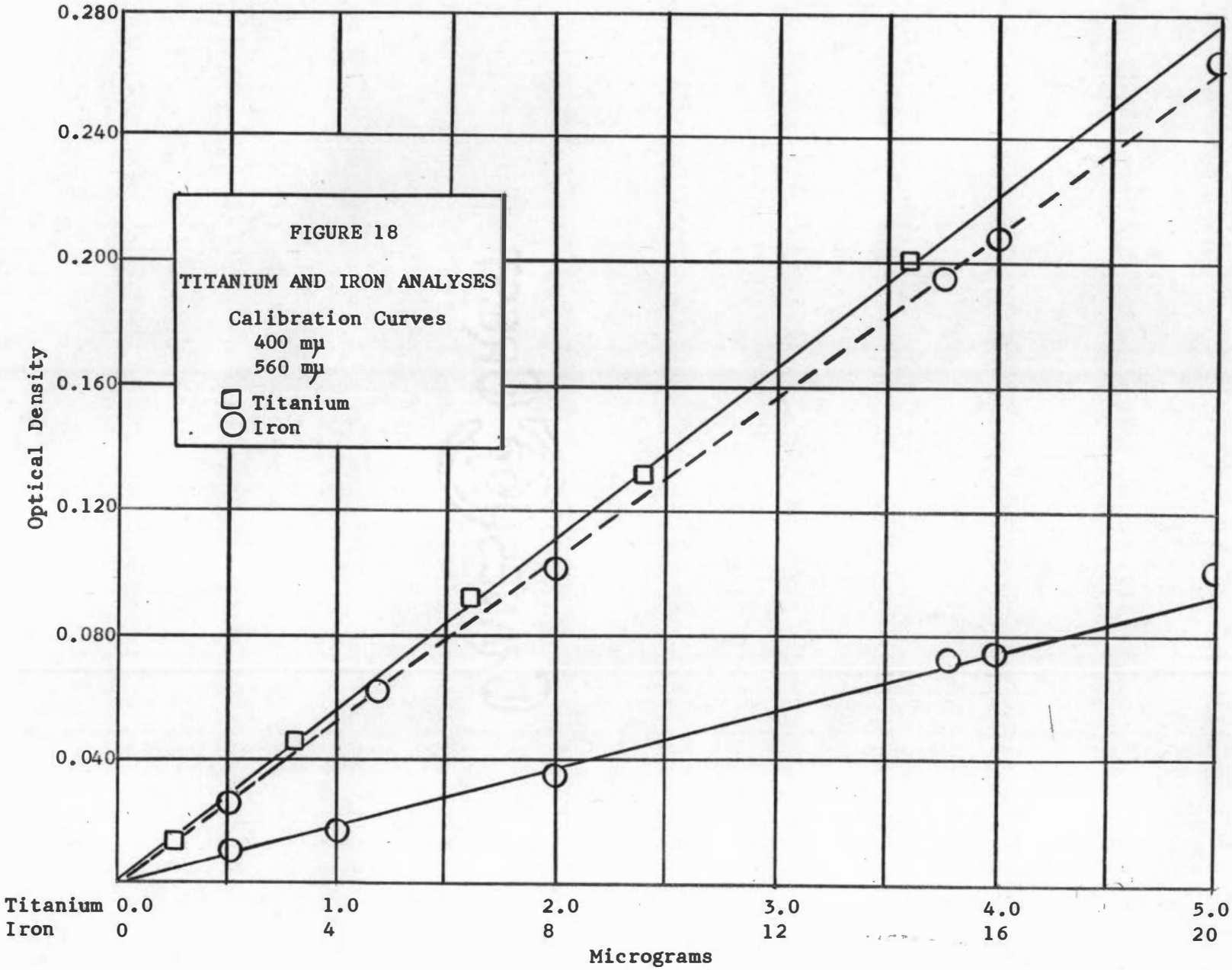


FIGURE 18
TITANIUM AND IRON ANALYSES
Calibration Curves
400 mμ
560 mμ
Titanium
Iron
Optical Density
0.280
0.240
0.200
0.160
0.120
0.080
0.040
Titanium 0.0 1.0 2.0 3.0 4.0 5.0
Iron 0 4 8 12 16 20
Micrograms

Subsequent work indicated that the interference was not from iron, but was probably due to copper. This metal also complexes with Tiron, and a spectrophotometric method has been developed recently.[42] The source of contamination was probably the brass mounting block on which the titanium disc was cemented. After the sample was remounted on aluminum, which does not interfere except at high concentrations, no further difficulty was experienced.

C. Cadmium

1. Analytical Method

The standard procedure which has been used with other metals was used to determine the rate of soap desorption from the cadmium sample surface. The analytical method for the determination of cadmium was adapted from that of Saltzman.[43] Dithizone is the colorimetric reagent in this method.

The following reagents were prepared:

a. Primary standard. In a 250-ml. volumetric flask, 0.2500 g. of cadmium metal was dissolved with 5 ml. of concentrated nitric acid. The solution was diluted to the mark with deionized water.

b. Secondary standard. A secondary standard was prepared by diluting 2.00 ml. of primary standard to 250 ml. with 0.1 N. hydrochloric acid.

c. Tertiary standard. A tertiary standard, containing 0.4 /ml., was prepared by diluting 5.00 ml. of secondary standard to 100 ml.

d. Standard dithizone solution. Eight milligrams of diphenylthiocarbazone (dithizone) was dissolved in 1 liter of chloroform. This solution was kept in a refrigerator.

e. Chloroform. Fisher's Certified Reagent, which was "suitable for use in dithizone test," was used.

f. Hydroxylamine hydrochloride. Twenty milligrams of hydroxylamine hydrochloride was dissolved in 100 ml. of deionized water.

g. Sodium hydroxide. A 40 per cent sodium hydroxide solution was prepared and stored in a polyethylene bottle.

2. Procedure

According to Saltzman, stable colors are obtained and decomposition losses reduced by using hydroxylamine hydrochloride in the extraction and minimizing the contact time between the alkali and chloroform solutions.

The proper amounts of tertiary standard (0-4γ) were pipetted into graduated cylinders, and the volume adjusted to 15 ml. with 0.1 N. hydrochloric acid. Then 0.25 ml. of hydroxylamine hydrochloride solution and 5.00 ml. of 40 per cent sodium hydroxide were added. Just before the samples were ready for analysis, 20 ml. of dithizone solution was pipetted into the cadmium solution, and the mixture shaken for one minute. Upon separation, most of the lower chloroform layer was pipetted from the cylinder and into a 25-ml. volumetric flask where it was allowed to stand for thirty minutes. Its optical density was then determined, using 5-cm. cells with a Beckman DU spectrophotometer at a wavelength of 518 mμ.

The calibration curve obtained for the cadmium-dithizone method is shown in Figure 19. For the desorption rate determination, the samples were machined under "U" solution, exposed to "U" for fifteen minutes, then transferred to fresh "U" solutions for varying exposure times. The cadmium was extracted from the cyclohexane with two 7.5-ml. portions of 0.1 N. hydrochloric acid. The procedure was then identical with that of the standard solutions.

D. Vanadium

1. Analytical Method

The most suitable analytical method for trace quantities of vanadium appears to be the phosphotungstate method.[44] A yellow "soluble" phosphotungstovanadic acid is formed by the addition of phosphoric acid and sodium tungstate to an acid vanadate solution.

The following reagents were prepared:

a. Sodium tungstate. A solution was prepared by dissolving 16.5 g. of reagent grade sodium tungstate dihydrate in 100 ml. of deionized water.

b. Phosphoric acid. A 1:2 phosphoric acid solution was prepared.

c. Sodium persulfate. Ten grams of sodium persulfate was dissolved in 100 ml. of deionized water.

d. Vanadium standards. A primary vanadium standard was prepared by dissolving 0.2500 g. of vanadium metal in 5 ml. of concentrated nitric acid and diluting to 250 ml. Secondary and tertiary standards containing 8 γ/ml. and 0.8 γ/ml. were prepared by dilution with 0.5 N. sulfuric acid.

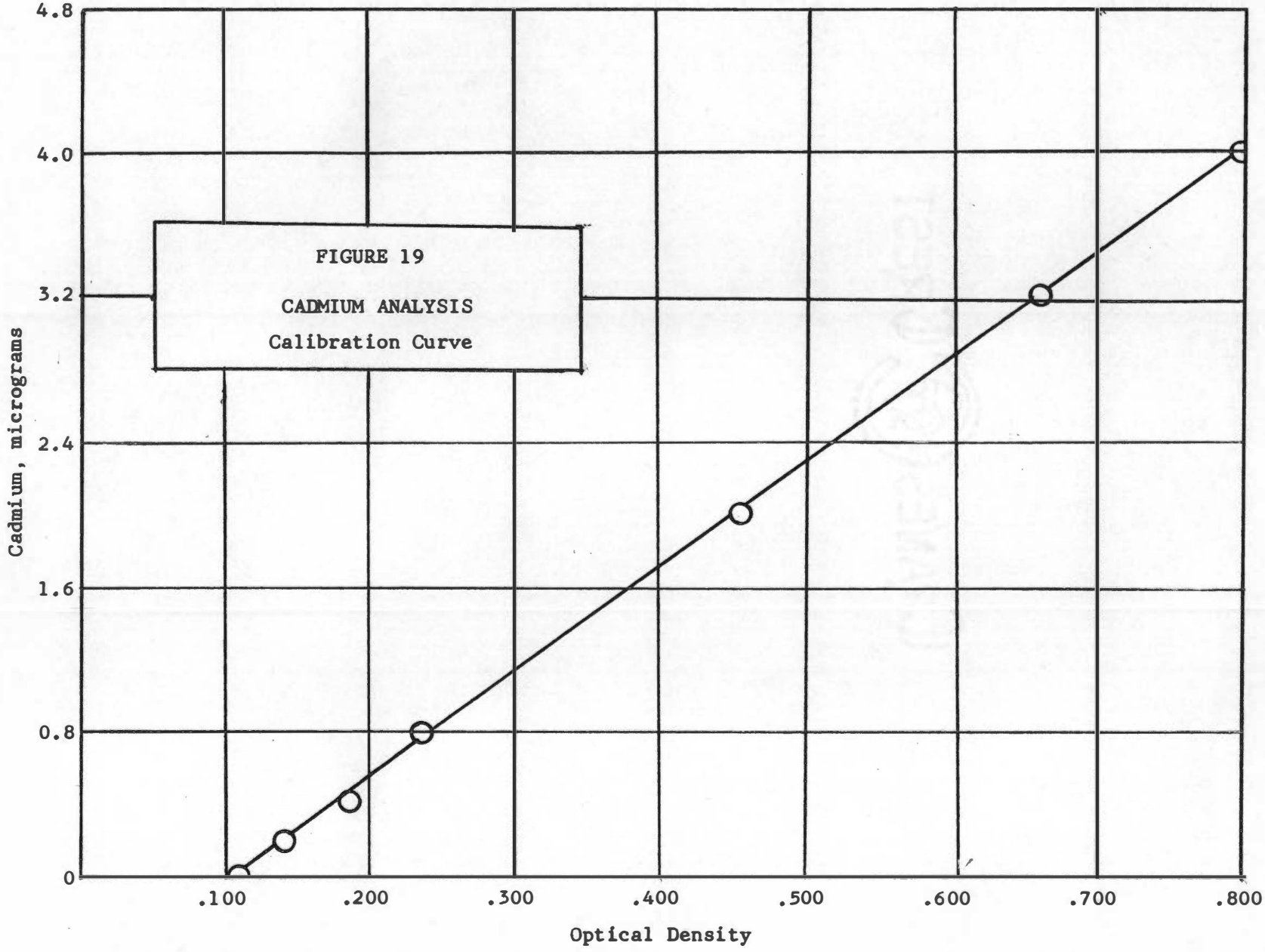


FIGURE 19

CADMIUM ANALYSIS

Calibration Curve

2. Procedure

The appropriate amounts of standard solutions were pipetted into a graduated cylinder, and the volume adjusted to 15 ml. with 0.5 N. sulfuric acid. Then 1.0 ml. of phosphoric acid solution and 0.5 ml. of sodium persulfate solution were added. The samples were allowed to stand overnight. After 0.5 ml. of sodium tungstate solution was added, the samples were allowed to stand thirty minutes before the optical density was determined at 400 mμ. The calibration curve is shown in Figure 20.

The usual procedure for determining the desorption rate of vanadium was used. Samples were extracted with two 7.5-ml. portions of 0.5 N. sulfuric acid, and the phosphotungstate method was used as described.

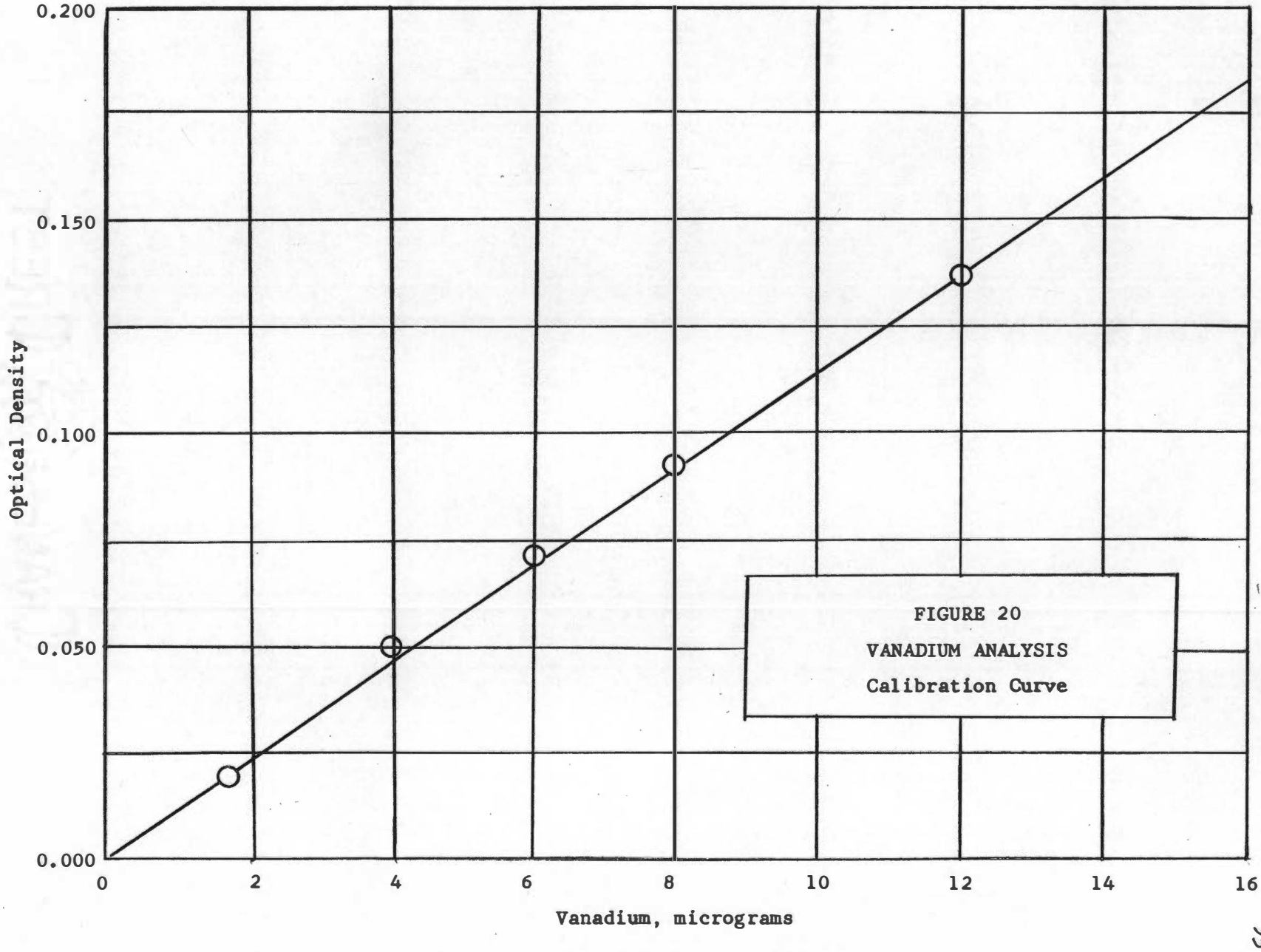


FIGURE 20
VANADIUM ANALYSIS
Calibration Curve

APPENDIX III

THE STATISTICS OF RADIOACTIVITY MEASUREMENTS

Nuclear disintegration is a random phenomenon and may be treated by established statistical principles. The brief discussion presented here is from the more complete treatment of Friedlander and Kennedy.[45]

In recording a certain count over a period of time an average count is obtained. The value is defined as,

$$\bar{x} = \frac{1}{N_o} \sum_{i=1}^{i=N_o} x_i \quad ,$$

where N_o is the number of values of x to be averaged. A knowledge of the statistical dependability is usually desired. That is, it is advantageous to know how much each value differs from the average. This is sometimes expressed as the dispersion, σ_x^2, which is defined as,

$$\sigma_x^2 = \frac{1}{N_o} \sum_{1}^{N_o} (x_2 - \bar{x})^2 \quad .$$

The square root of the dispersion, σ_x, is more commonly used. This is called the standard deviation.

When a large number of radioactive atoms are observed for a short period relative to their half-life, the probability of observing a given value can be shown to follow the Poisson distribution:

$$W(m) = \frac{M^m e^{-M}}{m!} \quad .$$

$W(m)$ is the probability of observing a certain number of counts, m, and M is the expected average. For Poisson distributions, the standard

deviation is equal to the square root of the average number of counts; that is,

$$\sigma = \sqrt{M} \quad .$$

An important consideration in adding or subtracting counting results is the effect on the standard deviation. The sum of two Poisson distributions gives another Poisson distribution, so the dispersion is the sum of the individual dispersions. Thus,

$$\sigma_s^2 = \sigma_1^2 + \sigma_2^2 + \ldots \quad .$$

The difference of two Poisson distributions is not a Poisson distribution, but the resulting dispersion is the sum of the individual dispersions, or,

$$\sigma_d^2 = \sigma_1^2 + \sigma_2^2 \quad .$$

The standard deviation is not considered by many to be critical enough for radioactive measurements, so the error is often expressed as the reliable error, E, which is the deviation which will be encountered no more than 10 per cent of the time. It is equal to 1.65 times the standard deviation.

In a typical monolayer measurement, a count of about 1400 counts/min. was counted for fifteen minutes, and the background of 90 counts/min. also was counted for fifteen minutes. The reliable error would be in terms of counts per minutes:

$$\frac{E}{t} = \frac{1.65\sigma_d}{t} = \frac{\sqrt{1400(15) + 90(15)}}{15} = 16 \text{ counts/min.}$$

The reliable per cent error is, then,

$$\frac{16}{1400 - 90} \times 100 = 1.2 \text{ per cent} \quad .$$

For partial monolayers, the reliable error may run as high as 8 per cent. Over-all, however, the counting errors are well below the other experimental errors.

APPENDIX IV

ADSORPTION OF ALKYL ARYL SULFONATES

Some adsorption studies have been made on mixtures of alkyl aryl sodium sulfonates labeled with sulfur-35. These samples were supplied by Dr. Preston L. Gant of the Continental Oil Company of Ponca City, Oklahoma. Two commercial products, Bryton-HY and Sherosope F-430, were received, along with labeled synthetic mixtures with similar composition. The analyses of these products are listed in Table IX. The nature of these mixtures is best understood by a description of their preparation. The Bryton-HY was made from the product of an alkylation of benzene by a mixture of alkenes with an average molecular weight of dodecene. The high molecular weight product, which probably had highly branched chains, was sulfonated to give a mixture with essentially the same molecular weight range as the commercial Bryton-HY. Sherosope F-430 was obtained by the sulfonation of natural oils and was also a mixture of a wide range of molecular weights.

A stock solution, labeled "50B," was prepared by dissolving 0.1732 g. of Bryton-HY in 500 ml. of purified cyclohexane. Dilution of aliquots to one-fiftieth of this concentration gave a working solution, "B," which was 10.1×10^{-6} molar in sulfonate molecules. This corresponds closely to the concentration of "A," which was 8.83×10^{-6} molar nonadecanoic acid.

TABLE IX

MIXED ALKYL ARYL SODIUM SULFONATE COMPOSITIONS

	Bryton-HY		Sherosope F-430	
	Labeled	Unlabeled	Labeled	Unlabeled
Combining weight	477	482	435	452
Per cent sulfonate	69.8	62.4	69.9	62.6
Per cent oil	30.2	34.4	30.1	29.1
Per cent H_2O	--	3.1	--	7.3
Per cent Na_2SO_4	--	0.42	--	0.5

A. Radiochemical Standardization

Radiochemical standardization by pipetting 0.50 ml. of "B" onto freshly machined surfaces gave excellent results with 1020 steel, but the reproducibility on a copper surface was extremely poor. The concentration of molecules on the sample surface of 11.4 sq. cm. area was calculated to be:

$$\frac{0.50 \text{ ml.} \times 10.1 \times 10^{-9} \text{ moles/ml.} \times 6.02 \times 10^{23} \times 100 \text{ Å}^2}{11.4 \times 10^{16} \text{ Å}^2} = 2.68 \text{ molecules per } 100 \text{ Å}^2.$$

For 1020 steel, the average count for this concentration was found to be 550 counts/min.

Since the radioactive material apparently did not deposit uniformly on the copper surface, a small disc 1 inch in diameter was machined on the sample surface. This exactly fit the mask of the counter tube, so all of the material was counted, regardless of whether it was uniformly distributed. A smaller amount, 0.25 ml., was pipetted onto the smaller area. This gave a concentration of 3.01 molecules per 100 $Å^2$. Good reproducibility was obtained, and an average count of 658 counts/min. was found.

B. Adsorption Measurements

1. 1020 Steel

Adsorption of the sulfonate was determined by end-milling the 1020 steel sample under solution "B" and exposing the sample to a stirred solution of "B" for varying times. The results with Bryton-HY

on 1020 steel are tabulated below. Measurements were also made with "4B," a solution four times the concentration of "B."

Time, minutes	B		4B	
	Counts/min.	Molecules per 100 Å^2	Counts/min.	Molecules per 100 Å^2
5	109	0.53		
15	294	1.43	293	1.43
30	372	1.81	361	1.76
60				
120	381	1.86	393	1.92
180			409	1.99
200	396	1.92		
310	372	1.82		
350			414	2.02
360			422	2.06
500				
600	409	1.99		

Solutions "50F" and "F" having the same molarity as "50B" and "B" were prepared from the Sherosope F-430 radioactive sample. Radiochemical standardization yielded an average value of 275 counts/min. for a surface concentration of 2.68 molecules per 100 Å^2. The following is a tabulation of adsorption of "F" on 1020 steel.

Time, minutes	Count	Molecules per 100 Å^2 of Geometric Area
15	136	1.80
30	188	1.82
60	215	2.09
180	246	2.39
270	215	2.09
360	265	2.57

It should be realized that the sulfonates are sodium salts, not free acids. Furthermore, the hydrocarbon chains are branched to an unknown extent and probably not in all molecules to the same degree.

The precision of the F-430 measurement was reduced by the low specific activity, hence the small count. Roughly, however, there appears to be little difference in the amount of adsorption of Bryton-HY and Sherosope F-430. Assuming a unit roughness factor, the area per molecule would be 40-50 $Å^2$. This appears rather high, but, since the molecules are highly branched, it is possible that a monolayer was formed.

2. Copper

The following adsorption data were observed with Bryton-HY on copper:

Time, minutes	B		4B	
	Counts/min.	Molecules per 100 $Å^2$	Counts/min.	Molecules per 100 $Å^2$
15	151	0.69	164	0.74
60			168	0.77
120			151	0.69
180	165	0.75		

The area per molecule assuming unit roughness is about 130 $Å^2$.

C. Exchange Measurements

Radioactive exchange determinations were made with Bryton-HY on 1020 steel. An unlabeled stock solution, designated "50BU," was prepared. It corresponded closely to the sulfur-35 labeled stock solution, "50B"; both solutions have the same sulfonate concentration.

In preparing solution "50BU," 0.0388 g. of unlabeled Bryton-HY was dissolved in 100 ml. of cyclohexane. An effort was made to co-distil the water contained in the sulfonate by evaporating the sample on a hot plate down to about 25 ml. Then it was diluted back to about 100 ml.

and evaporated again to about 25 ml. The sample was then diluted to exactly 100 ml. A solution of "BU" was prepared by diluting solution "50BU" fifty-fold.

The exchange measurements were made as follows. The sample was machined and exposed for a total time of sixty minutes under solution "BU." This longer time was used instead of the standard time of fifteen minutes which was employed with nonadecanoic acid, because it takes longer for the saturation level to be reached. After sixty minutes exposure to "BU," the steel sample was transferred to a stirred solution of labeled sulfonate solution, "B," for varying exposure times. The results are tabulated below.

Time, minutes	Counts/min.
30	9
60	25
120	216
270	333
1000	352

Apparently there was a very slow pick-up of the radioactive material.

The reverse of the above experiments was also run. The sample was machined and exposed under "B" for sixty minutes, then transferred to "BU" solutions for varying times. The results were:

Time, minutes	Counts/min.
60	326
120	414
180	309
270	352
1000	261

While the reproducibility of these results is disappointingly poor, it is clear that very little of the originally adsorbed material is desorbed. It is obvious that "B" and "BU" do not behave the same way and are not equivalent. Perhaps the traces of water or sodium sulfate in "BU" are responsible. It would be necessary to work with material of more definite composition before this point could be definitely explained.

APPENDIX V

PRELIMINARY EXPERIMENTS WITH ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY

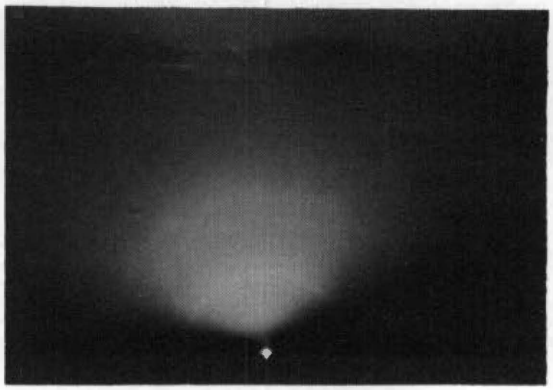
The electron diffraction camera and the electron microscope have been used to examine some surfaces produced by the techniques used in this research. Samples of copper were machined under air, pure solvent, and nonadecanoic acid solution for these preliminary experiments. From these samples, Mr. Warren W. Harris of the Oak Ridge Gaseous Diffusion Plant Laboratories of the Union Carbide Nuclear Company has obtained the electron diffraction patterns and electron photomicrographs which are shown in Figures 21 and 22.

A. Electron Diffraction

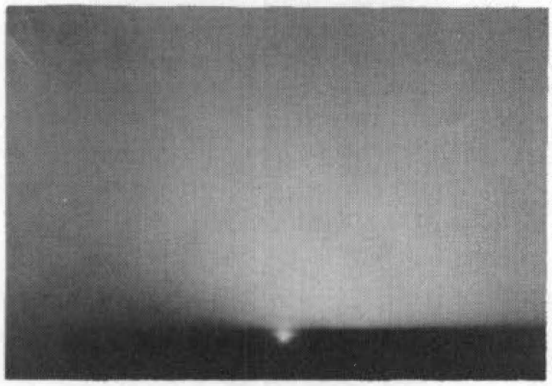
Useful information concerning surface roughness can be obtained from electron diffraction methods. Sharp diffraction patterns are produced not by reflection from the main surface, but by refraction in the small protuberances which extend from the surface. When the incident electron beam is passed parallel to the surface, a pattern is observed if a few prominent peaks are present even on a relatively smooth surface.

Considerable detail has been lost in the photography and reproducing processes used in preparing Figure 21. Nevertheless, the following observations were made. Air-machined copper produces distinct arcs (Figure 21A). These correspond with the pattern of copper oxide. Very little pattern is detectable with the solvent-machined sample, which

A. Air-Machined Copper



B. Solvent-Machined Copper



C. Solution-Machined Copper

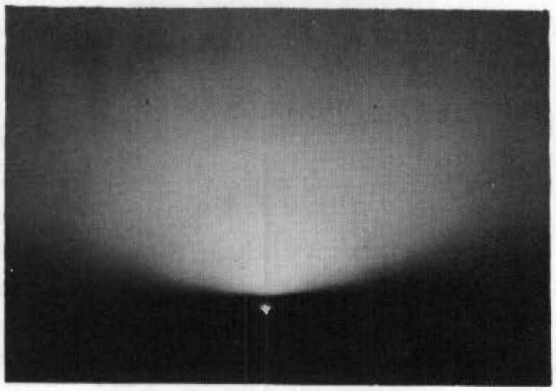
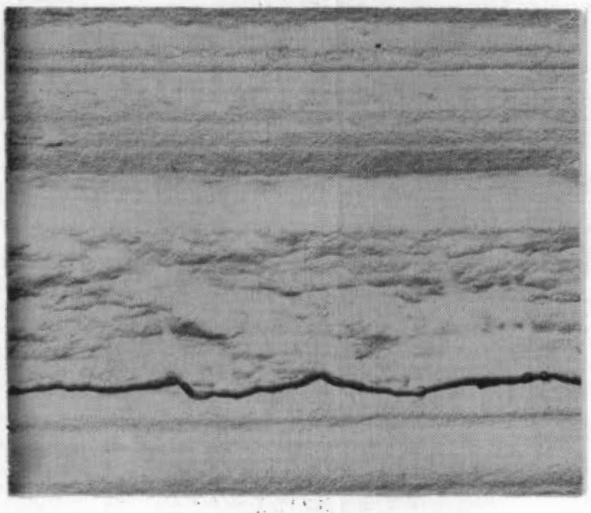


FIGURE 21

ELECTRON DIFFRACTION PATTERNS

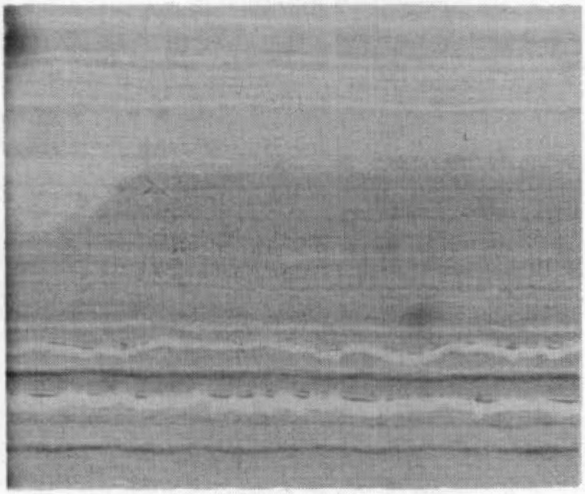
A. Air-Machined Copper

Magnification: 20,000



B. Solvent-Machined Copper

Magnification: 20,000



C. Solution-Machined Copper

Magnification: 18,000

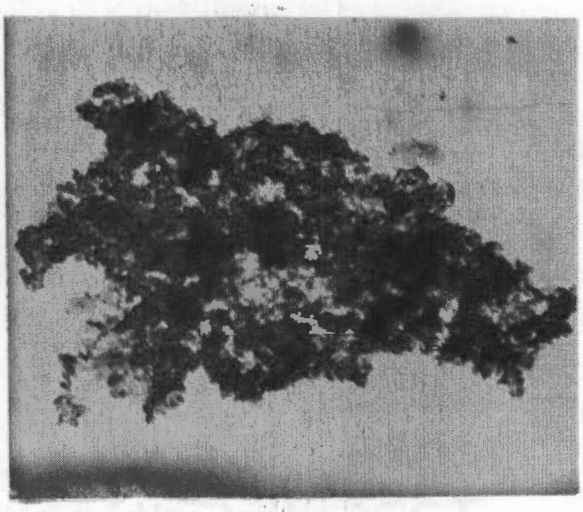


FIGURE 22

ELECTRON MICROPHOTOGRAPHS

indicates that the surface is extremely smooth. Protuberances of a height of 25 Å should have been sufficient to yield good lines. The diffraction pattern observed on the solution-machined sample (Figure 21C) is believed to be due to a partially oriented adsorbed monolayer.

B. Electron Microscopy

The high resolving power of the electron microscope makes it a valuable instrument for the determination of surface roughness. The smoothness of machined copper samples is shown by the electron photomicrographs in Figure 22. The air-machined and solvent-machined samples were shadowed with gold at a 10 to 1 ratio. Silica replicas were made of all three specimens. On the solvent-machined surface the maximum observed shadow is about 2 mm. This would correspond to a ridge only about 100 Å high. The majority of the solvent-machined surface is much smoother than this. Considerable roughening of the air-machined surface is observable. This is believed to be due to the heavy oxide formation.

The spots shown in Figure 22C were observed on a solution-machined sample which had been exposed to air for about thirty days before the photomicrograph was made. The sample was not shadowed. The nature of these dark spots is not known, but they might be due to the coagulation of the soap film upon aging. It is also possible they are caused by extraneous material.

The work reported was only of an exploratory nature. It is expected that further investigation will be useful in confirming or revising these preliminary conclusions.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. F. P. Bowden and J. E. Young, Nature, 164, 1089 (1949).

2. E. Rabinowicz and D. Tabor, Proc. Roy. Soc., A208, 455 (1951).

3. H. S. Taylor, Proc. Roy. Soc., A108, 105 (1925).

4. H. A. Smith and K. A. Allen, J. Phys. Chem., 58, 499 (1954).

5. R. M. McGill, "The Adsorption of n-Nonadecanoic Acid on Mechanically Activated Metal Surfaces," Doctoral Dissertation, The University of Tennessee, Knoxville, Tennessee, December 1955.

6. T. Fort, "Some Properties of Surface Films Formed by Adsorption of n-Nonadecanoic Acid on Mechanically Activated Metal Surfaces," Doctoral Dissertation, The University of Tennessee, Knoxville, Tennessee, June 1957.

7. I. Langmuir, J. Am. Chem. Soc., 39, 1848 (1917).

8. N. K. Adam, "The Physics and Chemistry of Surfaces," 2nd Ed., Oxford University Press, London, England, 1938, pp. 47, et. seq.

9. W. C. Bigelow, D. C. Pickett, and W. A. Zisman, J. Colloid Sci., 1, 513 (1946).

10. W. C. Bigelow, E. Glass, and W. A. Zisman, J. Colloid Sci., 2, 563 (1947).

11. H. A. Pohl, M. E. Hobbs, and P. M. Gross, Ann. N. Y. Acad. Sci., 40, No. 5, 389 (1940).

12. J. J. Frewing, Proc. Roy. Soc., A183, 270 (1944).

13. E. Cook and N. Hackerman, J. Phys. and Colloid Chem., 55, 549 (1951).

14. H. A. Smith and J. F. Fuzek, J. Am. Chem. Soc., 68, 229 (1946).

15. L. O. Brockway and J. Karle, J. Coll. Sci., 2, 277 (1947).

16. H. T. Epstein, J. Phys. and Colloid Chem., 54, 1053 (1950).

17. R. T. Mathieson, Nature, 183, 1803 (1959).

18. H. D. Cook and H. E. Ries, Jr., J. Phys. Chem., 63, 226 (1959).

19. O. Levine and W. A. Zisman, Abstracts of Papers, 132nd Meeting of the American Chemical Society, New York, N. Y., September 8-13, 1957, p. 9-I.

20. A. Dobry, Lubrication Eng., July-August 1954, taken from Research Report R-94603-2-H, Westinghouse Research Laboratories, March 1954.

21. F. P. Bowden and A. C. Moore, Trans. Faraday Soc., 47, 900 (1951).

22. D. E. Beischer, J. Phys. Chem., 57, 134 (1953).

23. J. W. Shepard and J. P. Ryan, J. Phys. Chem., 63, 1729 (1959).

24. J. Kramer, Z. Phys., 125, 739 (1949).

25. H. A. Smith and T. Fort, J. Phys. Chem., 62, 519 (1958).

26. W. A. Zisman, J. Chem. Phys., 9, 534 (1941).

27. W. F. Libby, "Radiocarbon Dating," University of Chicago Press, Chicago, Ill., 1952.

28. R. M. Lemmon, Nucleonics, 11, No. 10, 44 (1953).

29. H. H. Seliger, Phys. Rev., 88, 408 (1952).

30. L. Yaffe and K. L. Justus, J. Chem. Soc., 341 (1949).

31. R. G. Baker and L. Katz, Nucleonics, 11, No. 2, 14 (1953).

32. J. J. Bikerman, "Surface Chemistry," 2nd Ed., Academic Press, Inc., New York, N. Y., 1958, p. 274.

33. R. C. Mehrota and K. C. Pande, J. Inorg. and Nuclear Chem., 2, 60 (1956).

34. A. Gilmour, A. Jobling, S. M. Nelson, J. Chem. Soc., 1972 (1956).

35. W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 281.

36. W. G. Dauben, J. C. Reid, and P. E. Yankwich, Anal. Chem., 19, 828 (1947).

37. R. L. Bennett and H. A. Smith, Anal. Chem., 31, 1441 (1959).

38. C. L. Luke, Anal. Chem., 28, 1276 (1956).

39. F. Feigl, "Spot Tests," Vol. I, "Inorganic Applications," 4th Ed., Elsevier Publishing Co., New York, N. Y., 1954, p. 109.

40. J. H. Yoe and A. R. Armstrong, Anal. Chem., 19, 100 (1947).

41. P. Szarvas and B. Csiszar, Magyar Kem. Folyoirat, 61, 50 (1955); C. A., 49, 15619 (1955).

42. A. K. Majumdar and C. P. Savariar, Anal. Chem. Acta, 21, 53 (1959).

43. B. E. Saltzman, Anal. Chem., 25, 493 (1953).

44. E. R. Wright and M. G. Miller, Ind. Eng. Chem. Anal. Ed., 9, 251 (1953).

45. G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 252-270.

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